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Correlations for the Determination of Surface Diffusivities of Organic Chemicals Adsorbed onto Granular Activated Carbon

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CORRELATIONS FOR THE DETERMINATION OF SURFACE DIFFUSIVITIES OF ORGANIC CHEMICALS ADSORBED ONTO GRANULAR ACTIVATED CARBON

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

In treating drinking water to remove synthetic organic chemicals, granular activated carbon is used. The research reported here considers the surface diffusivities of organic chemicals adsorbed onto granular activated carbon.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

Differential column batch reactor (DCBR) experiments in organic-free water were conducted for the following volatile organic compounds (VOCs): trichloroethene, tetrachloroethene, cis-1,2 dichlorethene, and toluene. Surface diffusion was required to explain the rate of uptake for the VOCs, and the contribution of pore diffusion was determined to be negligible. Since considerable time is required to conduct a DCBR study, a correlation was developed for the surface diffusion based on the liquid diffusivity of the adsorbates and the physical properties of the activated carbon. The correlation can be used to calculate the surface diffusivities of halogenated one- and two-carbon molecules and some aromatic substituted organic compounds for two types of carbons. The significance of this correlation is that it can be used to calculate the mass transfer zone lenghts of VOCs in a fixed-bed adsorber with a fair amount of precision.

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I. INTRODUCTION

Treatment with granular activated carbon (GAC) is a useful, but expensive technique for removal of synthetic organic chemicals (SOCS) found in drinking water sources. A properly designed fixed-bed adsorption is required in order to reduce the cost of using GAC. A pilot investigation and a predictive model can be used to design a fixed-bed process. A pilot investigation is only valid for the duration of the study. A predictive model and a pilot investigation, however, allows a user to design fixed-bed adsorbers for treatment conditions other than the original pilot investigation. The HSDM (Homogeneous Surface Diffusion Model) has been shown to successfully predict fixed-bed adsorber dynamics for a number of adsorbate-adsorbent systems (Crittenden, 1978; Lee, 1980; Thacker, 1983; and Pirbazari, 1981). The important kinetic parameters in the HSDM are the liquid-phase mass transfer coefficients and the intraparticle diffusion coefficients. The liquid-phase mass transfer coefficients are estimated using various correlations (Williamson _et. al._,1963; Wilson and Geankoplis, 1966). The intraparticle diffusion coefficients are determined from differential column batch reactor (DCBR) studies. The DCBR studies, however, are difficult to conduct. Therefore, a correlation which was based on the liquid diffusivity and the physical properties of the carbon, was developed.

A correlation, which is based on the liquid diffusivities of the adsorbates and the void fraction of the activated carbons, can be used to estimate surface diffusion diffusivities of halogenated, one and two carbon molecules, and some aromatic substituted organic compounds. The correlation, however, is only valid for several macroporous activated carbons. The correlation can be used in conjunction with Hand et. al.; 1984 to calculate the mass transfer zone lengths (MTZL) for these types of compounds and activated carbons. To make conservative estimates for fixed-bed design, Equation VIII-13 may be used to estimate the surface diffusivity of a variety of adsorbates. Equation VIII-13 either predicts the surface diffusivity with reasonable precision or a lower surface diffusivity for some compounds. Consequently, the calculated surface diffusivity can be used to make a conservative estimate of the mass transfer zone lengths in a fixed-bed. This estimate would be conservative, because the surface diffusivity would either be correct or underestimated such that there would not be premature breakthrough of the solute in the fixed-bed.

Single-solute intraparticle diffusion coefficients for trichloroethene, tetrachloroethene, toluene, and cis-1,2 dichloroethene in organic-free water, along with single-solute trichloroethene in a background water matrix of total organic carbon (TOC) were measured. Surface diffusion was found to be the most important intraparticle mass transfer mechanism for single-solutes in organic-free water. Pore diffusion was slower than surface diffusion and did not predict the experimental data. The uptake rates for trichloroethene in the background water matrix and the organic-free water were the same, so competitive effects from the background water matrix were not observed.

A multicomponent batch rate study was attempted, but problems with degradation of the aromatic compounds occurred. Also, selection of a proper carbon dosage to determine surface diffusivities was not possible. If a high carbon dosage was chosen to observe the concentration history profile of the weakly adsorbing solute, it would result in a film transfer limited case for the strongly adsorbing solute. If a low carbon dosage was chosen to observe the concentration history profile of the strongly adsorbing solute, the concentration history for the weakly adsorbing solute would not be significantly depressed enough to see a profile and measurement of the intraparticle surface diffusion coefficient for the weakly adsorbing solute would not be possible.

II. EXPERIMENTAL PROCEDURES

A. Chemicals Used in Experiments

All chemicals used in single solute experiments were reagent grade or better. 1,1,1-trichloroethene, stabilized, (lot number 004411) and tetrachloroethene, (PCE), (Photrex), (lot number 2-9218) were obtained from J.T. Baker Chemical Company, Phillipsburg, New Jersey. 2,2,4-trimethylpentane, trihalomethane grade, (lot number AK716), trichloroethene, (TCE), (lot number AE777), and methyl alcohol, trihalomethane grade (lot number AL065) were obtained from Burdick and Jackson, Muskegon, Michigan. Cis-1,2 dichloroethene 97%,(DCE), (lot number 8409PK) and Toluene, 99%, (lot number 9115TH) were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin.

B. Carbons Used in Experiments

Two granular activated carbons were used in the studies: Calgon Corporation's Filtrasorb 400 (F-400) (lot number 52095) Pittsburgh, Pennsylvania, and Westvaco's WV-G (lot number 39815) Covington, Virginia, were used. Both carbons were originally 12x40 mesh. Ground Granular Activated Carbon (60 x 80 mesh) was also studied. For the (60 x 80 mesh) carbon, (12 x 40 mesh) carbon was ground until all of the original sample passed the 60 mesh size.

C. Water Matrices Used in Experiments

Two water matrices were used in these studies: Organic-free water was obtained from the Millipore system and raw water from well number four in Wausau, Wisconsin was the source of the other water matrix. The Millipore system consisted of a millipore Super-C cartridge, two ION-EX cartridges, and an Organex-Q cartridge in series. Finally, a Twin-90, 0.22μm, filter unit was used to eliminate microorganisms. To obtain organic-free water the Milli-Q water was purged. The city of Wausau, Wisconsin's well number 4 contained a mixture of various (VOCS) and total organic carbon (TOC) found in their drinking water source.

D. Carbon Preparation and Characterization

The granular activated carbons from the two manufacturers were obtained in two 50 pound bags. A representative sample was obtained by splitting the carbon. Both carbons were washed with purged Milli-Q water to remove any fine carbon particulate matter. The washings were continued until the supernatant was clear. The carbon was placed in an oven at 105°C for 12 hours. Finally, the carbon was placed in clean, brown, borosilicate bottles, with teflon liners, and stored in a dessicator. Appendix 4 contains the procedure for splitting and washing the carbon.

Both powdered granular activated carbon (PGAC), and ground granular activated carbon (GAC), were prepared by using a mortar and pestle to reduce the carbon particle size. The PGAC was used in the isotherm equilibrium studies and the GAC was used in the differential column batch rate studies. The carbon was placed in centrifuge bottles which were filled two-thirds full of purged Milli-Q water and capped. The bottles were shook and placed in a centrifuge. Again, the washings were continued until the supernatant was clear. The carbon was placed in an oven at 105°C for 16 hours. Finally, the carbon was placed in clean, brown, borosilicate bottles with teflon liners in the caps and stored in a dessicator. Appendix 4 contains the procedure for crushing and cleaning the carbon.

E. Chemical Analysis

Chemical analyses were made using the following instruments: 1) the Hewlett-Packard 5830A Gas Chromatograph upgraded to a 5840A with an electron capture detector 2) the Hewlett-Packard 5830A Gas Chromatograph with a flame ionization detector coupled with a Hewlett-Packard 7675A Purge and Trap Sampler. The columns which were used on the 5840A were either the 80/100 Carbopack B/0.1% SP-1000 or the 60/80 Carbopack C/0.2% Carbowax C. The column which was used on the 5830A was the 60/80 Carbopack B/1.0% SP-1000. All columns were 10 feet in length.

There were two analytical techniques which were used to measure the VOC samples. The first technique involved liquid-liquid extraction, using 2,2,4-trimethylpentane (isooctane) which contained an internal standard (1,1,1-trichloroethene). The procedure for extracting the sample was similar to the procedure which was described by Mieure (1977). Trichloroethene and tetrachloroethene were the compounds analyzed from the aqueous phase using this procedure. Once the VOC had been extracted with isooctane from the aqueous phase, the organic layer was injected into the Hewlett-Packard 5840A. The area ratios (sample area divided by the internal standard area), were used to determine the concentration. The determination of the correct extraction ratio was important to insure that a representative sample which can be accurately measured on the gas chromatograph. A sample calculation for the correct extraction ratio was shown by Johnson (1984).

The second technique used was the Purge and Trap. This technique was used for compounds that had poor response factors on the electron capture detector. The internal standard was 1,2 dichloropropane. A 10 ml aliquot of a water sample and a 5 ml aliquot of an internal standard were placed in a purge vessel which was attached to the Purge and Trap Sampler. The area ratios (sample area divided by the internal standard area), were used to determine the concentration.

F. Equilibrium Isotherm Procedure

The equilibrium studies which were performed used the bottle point procedure by Luft (1984). Serum bottles with various amounts of PGAC were allowed to come into contact with water containing the VOCS. Once equilibrium was attained, the serum bottle was centrifuged to separate the PGAC from the liquid. The liquid-phase concentration was determined by the liquid-liquid extraction technique.

G. Differential Column Batch Reactor Procedure

1. Previous Designs

Hand (1982) presented three possible experimental apparatus which could be used to measure the surface diffusivities of VOCS: the completely mixed batch reactor (CMBR), the Carberry reactor and the differential column batch reactor (DCBR). The CMBR consists of the GAC being dispersed in the aqueous phase. A motor controls a stirrer which agitates the liquid. The Carberry reactor is a modification of the CMBR. In this design, the carbon is fixed in a spinning basket. A motor rotates the basket in the fluid. The DCBR consists of a large reservoir, a pump, and a column packed with a differential height of carbon. The water from the reservoir is pumped through the fixed-bed of carbon and recycled into the reservoir.

2. Chosen Design to Conduct Kinetic Studies

The CMBR design does not work for soft carbons, since the impeller blades can cause attrition of the carbon particles and the smaller carbon particles would increase the adsorption rate. The Carberry reactor is a possible choice, but the user would have to use a large carbon dosage in this reactor.

However, the carbon dosages were small for the adsorbates of interest in this study. Therefore, the DCBR was chosen to conduct the experiments.

The procedure for the DCBR is presented in Appendix 5. The apparatus was constructed using glass, teflon, and stainless steel materials. These materials are chemically inert and therefore reduce the possibility of biased results due to system leaching and adsorption. A continuously mixed glass reaction vessel was completely filled with a water matrix and run at isothermal conditions. See Figure II-1 for the system design. For the single-solute runs in Milli-Q water, a pH of 6.0 was controlled using a phosphate buffer. The raw Wausau water matrix was not buffered, but the value of the pH was recorded and did not change during the experiment.

A high flowrate in the DCBR insured a minimum amount of liquid-phase mass transfer resistance. This allowed for better estimates of the surface diffusion coefficient for a given adsorbent-adsorbate system.

The liquid-phase concentrations at various times were measured and a concentration history profile for a given solute was obtained. The experimental data were compared to the mathematical models which characterize the process. The equations which describe the models are presented in sections III and IV.

Preliminary calculations and the criteria for the DCBR are contained in section V. This section allows a potential user to correctly perform the necessary calculations and to insure the experiment will yield a good estimate of the surface diffusion coefficient.

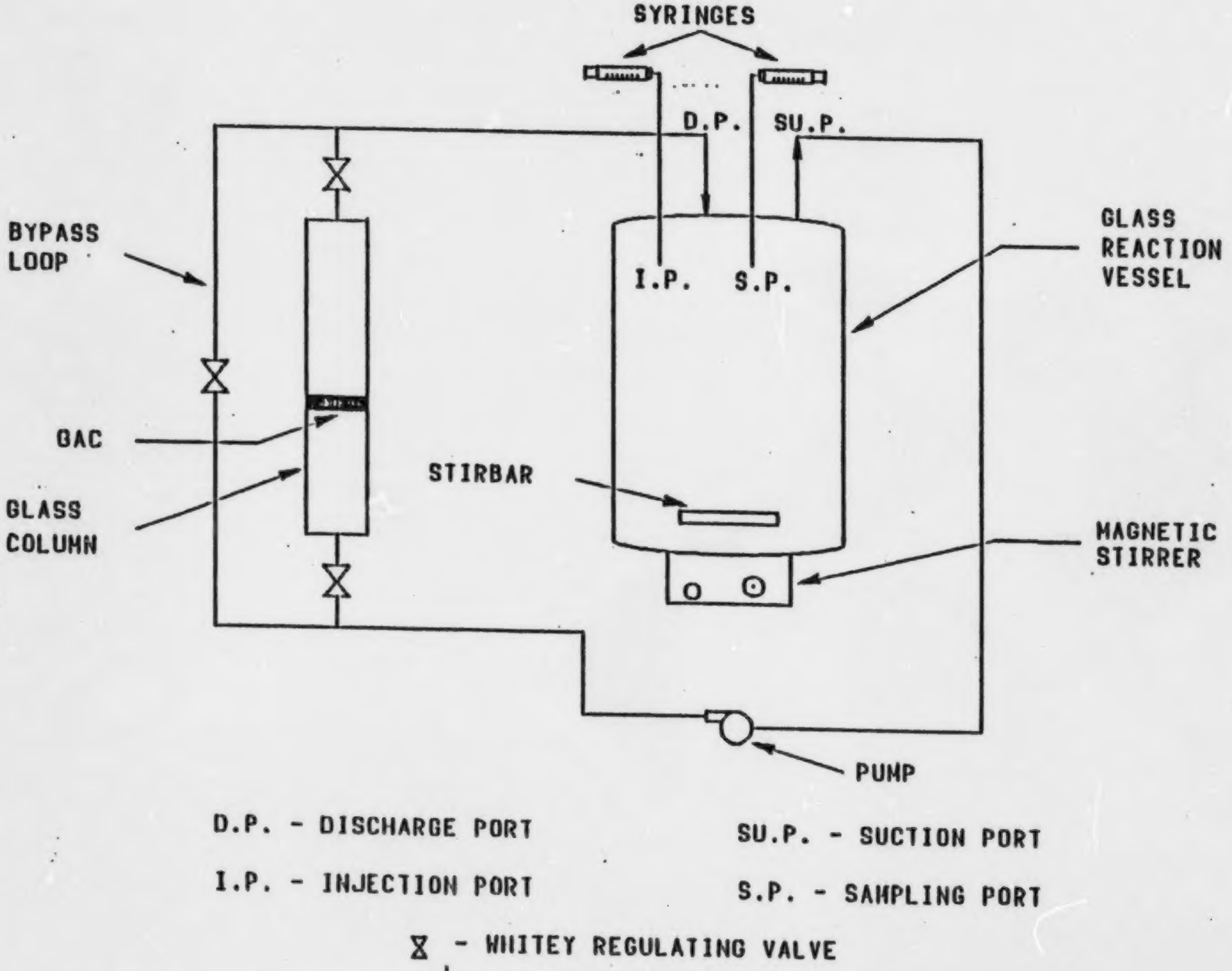

Figure II-1. Basic Design for the Differential Column Batch Reactor.

III. MODEL FRAMEWORK FOR THE BATCH HOMOGENEOUS SURFACE DIFFUSION MODEL

As shown in Figure III-1, a three step mechanism has been proposed to describe the adsorption of volatile organic compounds from solution into porous adsorbents such as granular activated carbon (GAC) (Weber et. al., 1963). The first step is the transport of the VOC from the liquid-phase to the exterior surface of the adsorbent. The second step is the diffusion of the VOC into the pores of the adsorbent and is comprised of both pore and surface diffusion. Finally, the third step are the local elementary reaction steps which are involved in the adsorption of VOCS. In the batch homogeneous surface diffusion model (BHSDM), the pore diffusion mechanism is neglected.

A. Previous Work

Several researchers have studied adsorption kinetics in batch reactors. Crittenden and Weber (1978), have independently measured intraparticle diffusion coefficients of phenol, p-toluene sulfonate, p-bromophenol, and dodecyl benzene sulfonate for model calibration and were able to predict adsorption column performance. Hand, Crittenden, and Thacker (1983), have provided user-orientated solutions to the batch homogeneous surface diffusion model which can be used to determine the surface diffusivity from differential column batch reactor studies. Suzuki and Kawazoe (1975) measured the single-solute adsorption rate from batch experiments of 15 volatile organic chemicals on coconut based carbon. Suzuki and Kawazoe (1974) also provided graphical solutions for batch reactors assuming that both pore or surface diffusion could describe the intraparticle mass transfer rate. van Lier (1983) conducted kinetic adsorption experiments with nitrobenzene on various types of carbon. He found that surface diffusion was the most important intraparticle diffusion mechanism. Sabin (1981) conducted kinetic

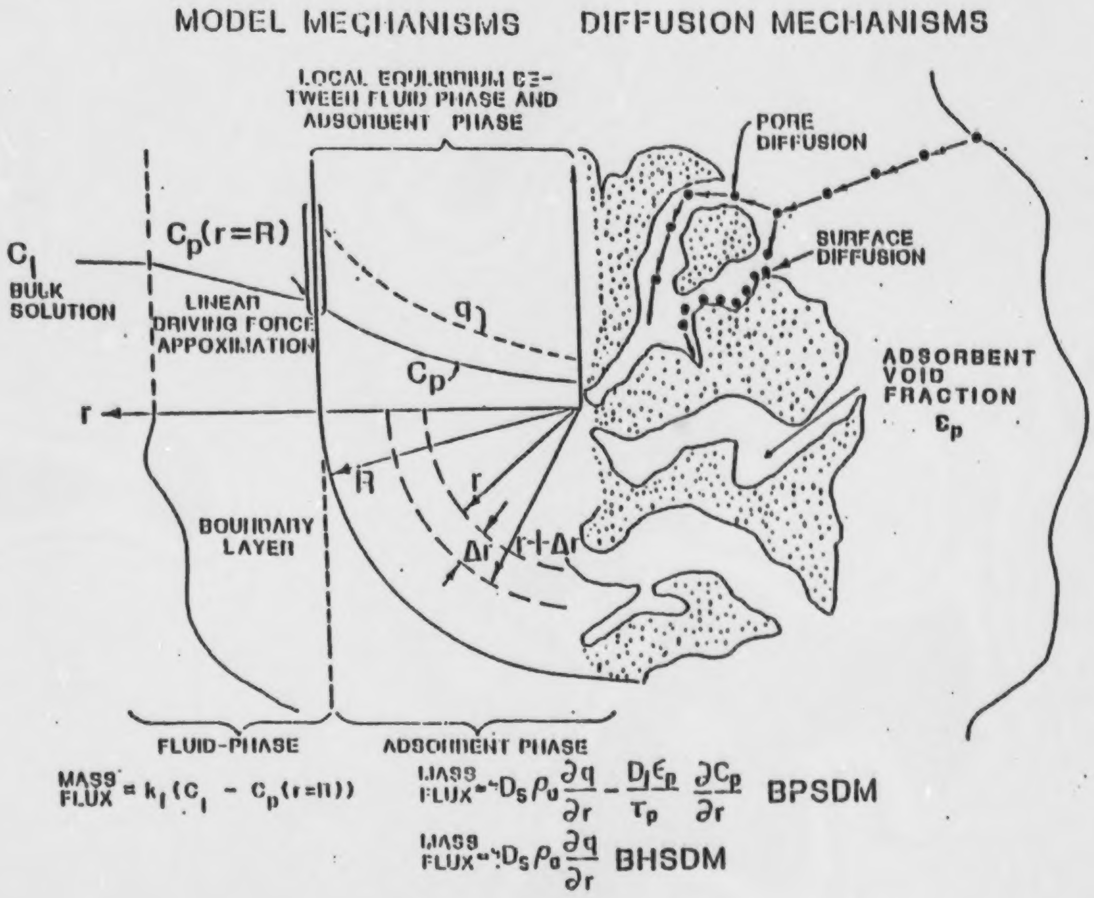
MODEL MECHANISMS
DIFFUSION MECHANISMS
LOCAL EQUILIBRIUM BE-TWEEN FLUID PHASE AND ADSORBENT PHASE
C_l
BULK SOLUTION
$C_p(r=R)$
LINEAR DRIVING FORCE APPOXIMATION
q
C_p
r
R
r
Δr
r+Δr
BOUNDARY LAYER
PORE DIFFUSION
SURFACE DIFFUSION
ADSORBENT VOID FRACTION ε_p
FLUID-PHASE
ADSORBENT PHASE
MASS FLUX = $k_l(C_l - C_p(r=R))$
MASS FLUX = $-D_s\rho_a\frac{\partial q}{\partial r} - \frac{D_l\varepsilon_p}{\tau_p}\frac{\partial C_p}{\partial r}$ BPSDM
MASS FLUX = $-D_s\rho_a\frac{\partial q}{\partial r}$ BHSDM

Figure III-1. Mechanisms and Assumptions that are Incorporated into the BHSDM and BPSDM.

adsorption experiments on two microporous carbons, HD-3000 and HD-4000, with chloroform and found that the surface diffusivities for the microporous carbons were lower than surface diffusivities for the macroporous carbon, F-400. See Table VIII-2 for the comparison.

B. Model Mechanisms and Assumptions

The multicomponent batch homogeneous surface diffusion model (BHSDM), includes the following transport mechanisms: 1) mass transfer from the bulk of the solution onto the outer surface of the particles, and 2) diffusion of molecules in the adsorbed state by surface diffusion. The BHSDM also includes the following assumptions: 1) the transport of adsorbate from the bulk solution to the exterior of the adsorbent particle is described by the linear driving force approximation, 2) at the exterior of the adsorbent particle, local equilibrium exists with the liquid-phase, 3) multicomponent adsorption equilibrium is described by ideal adsorbed solution theory (IAST, Radke and Prausnitz, 1972), while single-solute adsorption equilibrium is described by the Freundlich isotherm equation, 4) the intraparticle mass flux is described by Fick's law and bulk flow due to diffusion is neglected by assuming dilute solutions (Weber and Chakravorti, 1974), 5) surface diffusion describes the intraparticle mass flux, and 6) there are no solute-solute interactions in the diffusion process.

C. Equations Describing the Multicomponent BHSDM

Equations III-1 to III-7 describe the spatial and temporal variation of an adsorbate within the adsorbent and the liquid-phase. The derivation of these equations and their conversion into dimensionless form was presented by Friedman (1984). The following set of equations are required for obtaining solutions to the BHSDM:

The overall mass balance is:

$$0 = \frac{\partial \bar{C}_i(\bar{t}_s)}{\partial \bar{t}_s} + 3Dg_{s,i} \frac{\partial}{\partial \bar{t}_s} \int_0^1 \bar{q}_i(\bar{r},\bar{t}_s)\, \bar{r}^2 d\bar{r} \qquad \text{(III-1)}$$

where:

$$\frac{\partial \bar{C}_i(\bar{t}_s)}{\partial \bar{t}_s} = \text{Mass of Adsorbate i Accumulated in the Liquid Phase}$$

$$3Dg_{s,i} \frac{\partial}{\partial \bar{t}_s} \int_0^1 \bar{q}_i(\bar{r},\bar{t}_s)\, \bar{r}^2 d\bar{r} = \text{Total Mass of Adsorbate i in the Particle}$$

The initial conditions for equation III-1 are:

$$\bar{C}_i(\bar{t}_s = 0) = 1 \qquad \text{(III-2)}$$

$$\bar{q}_i(\bar{r},\bar{t}_s = 0) = 0 \qquad \text{(III-3)}$$

The intraparticle phase mass balance is:

$$\frac{D_{s,i}}{D_{s,max}} \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left[\bar{r}^2 \frac{\partial \bar{q}_i(\bar{r},\bar{t}_s)}{\partial \bar{r}} \right] = \frac{\partial \bar{q}_i(\bar{r},\bar{t}_s)}{\partial \bar{t}_s} \qquad \text{(III-4)}$$

where:

$$\frac{D_{s,i}}{D_{s,max}} \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left[\bar{r}^2 \frac{\partial \bar{q}_i(\bar{r},\bar{t}_s)}{\partial \bar{r}} \right] = \text{Mass of Adsorbate i Transferred Away from the Exterior Surface by Surface Diffusion}$$

$$\frac{\partial \bar{q}_i(\bar{r},\bar{t}_s)}{\partial \bar{t}_s} = \text{Mass of Adsorbate i Accumulated within the Adsorbent Particle}$$

The initial condition for Equation III-4 is:

$$\bar{q}_i(\bar{r},\bar{t}_s = 0) = 0 \qquad \text{(III-5)}$$

The boundary conditions for Equation III-4 are:

$$\frac{\partial}{\partial \bar{r}} \bar{q}_i(\bar{r} = 0, \bar{t}_s) = 0 \qquad \text{(III-6)}$$

$$\frac{\partial}{\partial \bar{t}_s} \int_0^1 \bar{q}_i(\bar{r}, \bar{t}_s)\, \bar{r}^2 d\bar{r} = Bi_{s,i} \frac{D_{s,i}}{D_{s,max}} \left[\bar{C}_i(\bar{t}_s) - \bar{C}_{p,i}(\bar{r}=1, \bar{t}_s) \right] \qquad \text{(III-7)}$$

For multicomponent mixtures, the nonlinear equation which couples Equations III-1 through III-7 is the IAST equation. Luft (1984) found that the IAST equation described competition for multicomponent mixtures. The IAST equation written in terms of i components and in dimensionless variables is:

$$\bar{C}_{p,i}(\bar{r}=1, \bar{t}_s) = \frac{\bar{q}_i(\bar{r}=1, \bar{t}_s) q_{e,i}}{\sum_{j=1}^{m} \bar{q}_j(\bar{r}=1, \bar{t}_s) q_{e,j}} \left[\frac{\sum_{k=1}^{m} n_k \bar{q}_k(\bar{r}=1, \bar{t}_s) q_{e,k}}{n_i q_{e,i}} \right]^{n_i} \qquad \text{(III-8)}$$

For single solutes, the Freundlich isotherm equation was used to relate the liquid-phase concentration at the exterior of the adsorbent to the adsorbent phase concentration.

Equations III-1 through III-8 contain two independent dimensionless variables: time, $\bar{t}_s$, and radial position, $\bar{r}$, and three dependent variables: liquid-phase concentration, $\bar{C}_i,(t_s)$, the solid phase concentration, $\bar{q}_i(r, t_s)$, and the liquid phase concentration at the exterior of the adsorbent $\bar{C}_p(r=1, t_s)$. These equations were solved by Friedman (1984) and his computer algorithms were used to determine the surface diffusivities.

D. Dimensionless Groups Which Describe the Multicomponent BHSDM

There are four independent dimensionless groups which characterize the solution to the BHSDM and determine if surface diffusion is the controlling mechanism in the differential column batch reactor study. The four independent dimensionless groups appearing in Equations III-1 to III-8 are: (a) $Dg_{s,i}$, which is the surface solute distribution parameter for component i based on surface diffusivity, (b) $D_{s,i}/D_{s,max}$, which is the ratio of the surface diffusivity for component i to the surface diffusivity of the fastest diffusing component, (c) $1/n_i$, which is a Freundlich isotherm constant for component i, and (d) $Bi_{s,i}$, which is the Biot number for component i is based on surface diffusivity. The surface solute distribution parameter which is based on surface diffusivity, $Dg_{s,i}$, and the Biot number which is based on surface diffusivity are defined as:

$$Dg_{s,i} = \frac{\rho_a q_{e,i}(1-\varepsilon)}{\varepsilon C_{o,i}} = \frac{Mq_{e,i}}{\varepsilon V C_{o,i}} \qquad \text{(III-9)}$$

$$Bi_{s,i} = \frac{k_{f,i}R(1-\varepsilon)}{D_{s,i}Dg_{s,i}\varepsilon} \qquad \text{(III-10)}$$

The surface solute distribution parameter, $Dg_{s,i}$, is the ratio of the mass of adsorbate i in the solid phase to the mass in the liquid-phase under equilibrium conditions. It was based on a single solute capacity and evaluated at the initial concentration of the batch reactor. As $Dg_{s,i}$ increases, the amount of adsorbate on the adsorbent increases. The surface Biot number, $Bi_{s,i}$, is the ratio of the liquid-phase mass transfer rate to the intraparticle phase mass transfer rate and has the greatest impact on the design of the DCBR. Hand, Crittenden, and Thacker (1984), have shown that for a $Bi_{s,i}$ greater than 30, the intraparticle phase mass transfer rate controls the mass transfer rate in fixed-beds. Therefore, it is possible to obtain better estimates of the surface diffusivity in a differential column batch reactor when the $Bi_{s,i}$ is greater than 30.

IV. MODEL FRAMEWORK FOR THE BATCH PORE AND SURFACE DIFFUSION MODEL

For a multicomponent mixture, the BHSDM may not predict the adsorption rate of both strongly and weakly adsorbing solutes. Both strongly and weakly adsorbing solutes can diffuse by two kinetic mechanisms: they can travel along the interior surface of the adsorbent or within the fluid contained in the void of the adsorbent. These two kinetic mechanisms are known as surface diffusion and pore diffusion, respectively. In the case of weakly adsorbing solutes, many of the active sites on the carbon walls are occupied by strongly adsorbing solutes and pore diffusion allows the weakly adsorbing solutes to continue to diffuse into the carbon particle. See Figure III-1. Therefore, a model incorporating both surface and pore diffusion as the intraparticle diffusion mechanism was developed by Friedman, (1984) and used in this study.

A. Previous Work

Several researchers have studied the combination of surface and pore diffusion. Suzuki and Kawazoe, 1974, have provided graphical solutions assuming both pore and surface diffusion could describe the intraparticle mass transfer rate. van Lier, 1983, conducted batch-wise experiments with a nitrobenzene/water/activated carbon system and tested several mathematical models. Fritz _et. al.,_ (1980) conducted competitive adsorption of p-nitrophenol/p-chlorophenol/activated carbon and p-nitrophenol/phenol/activated carbon systems. He found that the BPSDM predicted slightly better results than the BHSDM.

B. Model Mechanisms and Assumptions

The multicomponent batch pore and surface diffusion model (BPSDM) includes the following transport mechanisms: 1) mass transfer from the bulk solution onto the outer surface of the adsorbent particles, 2) diffusion of molecules in the adsorbed state known as surface diffusion, and 3) diffusion of molecules in the liquid filled pores known as pore diffusion. The BPSDM also includes the following assumptions: 1) transport of adsorbate from the bulk solution to the exterior of the adsorbent particle is described by the linear driving force approximation, 2) local equilibrium at a particular radial position is assumed throughout the adsorbent particle, 3) ideal adsorbed solution theory (Radke and Prausnitz, 1972; Luft, 1984) is used to describe the multicomponent equilibrium interactions, while single-solute adsorption equilibrium is described by the Freundlich isotherm equation 4) the intraparticle mass flux is described by Fick's law and bulk flow due to diffusion is neglected by assuming dilute solutions (Weber and Chakravorti, 1974), 5) surface and pore diffusion describes the intraparticle mass flux, and 6) there are no solute-solute interactions in the diffusion process.

C. Equations Describing the Multicomponent BPSDM

Equations IV-1 to IV-8 describe the spatial and temporal variation of an adsorbate within the adsorbent and the liquid-phase. To simplify the development of the equations for the BPSDM, the total loading of the particle, Y_i is expressed as the sum of the surface loading, q_i and the liquid-phase concentration in the pores, $C_{p,i}$ (Neretnieks, 1976; Fritz et. al., 1980).

$$Y_i(r,t) = q_i(r,t) + \frac{\varepsilon_p}{\rho_a} C_{p,i}(r,t) \tag{IV-1}$$

The derivation of these equations and their conversion into dimensionless form was presented by Friedman (1984). The following set of equations are required to obtain solutions to the BPSDM:

The overall mass balance is:

$$0 = \frac{\partial \bar{C}_i(\bar{t}_p)}{\partial \bar{t}_p} + 3Dg_i \frac{\partial}{\partial \bar{t}_p} \int_0^1 \bar{Y}_i(\bar{r},\bar{t}_p)\, \bar{r}^2 d\bar{r} \qquad \text{(IV-2)}$$

where:

$\frac{\partial \bar{C}_i(\bar{t}_p)}{\partial \bar{t}_p}$ = Mass of Adsorbate i Accumulated in the Liquid Phase

$3Dg_i \frac{\partial}{\partial \bar{t}_p} \int_0^1 \bar{Y}_i(\bar{r},\bar{t}_p)\, \bar{r}^2 d\bar{r}$ = Total Mass of Adsorbate in the Particle

The initial conditions for Equation IV-2 are:

$$\bar{C}_i(\bar{t}_p = 0) = 1 \qquad \text{(IV-3)}$$

$$\bar{Y}_i(\bar{r},\bar{t}_p = 0) = 0 \qquad \text{(IV-4)}$$

The intraparticle phase mass balance is:

$$\frac{1}{\bar{r}^2}\frac{\partial}{\partial \bar{r}}\left[\bar{r}^2 X_i \frac{\partial \bar{Y}_i(\bar{r},\bar{t}_p)}{\partial \bar{r}} + \bar{r}^2 Z_i \frac{\partial \bar{C}_{p,i}(\bar{r},\bar{t}_p)}{\partial \bar{r}}\right] = \frac{\partial \bar{Y}_i(\bar{r},\bar{t}_p)}{\partial \bar{t}_p} \qquad \text{(IV-5)}$$

where:

$\frac{1}{\bar{r}^2}\frac{\partial}{\partial \bar{r}}\left[\bar{r}^2 X_i \frac{\partial \bar{Y}_i(\bar{r},\bar{t}_p)}{\partial \bar{r}} + \bar{r}^2 Z_i \frac{\partial \bar{C}_{p,i}(\bar{r},\bar{t}_p)}{\partial \bar{r}}\right]$ = Mass of Adsorbate i Transferred Away from the Exterior Surface by Pore and Surface Diffusion

$\frac{\partial \bar{Y}_i(\bar{r},\bar{t}_p)}{\partial \bar{t}_p}$ = Mass of Adsorbate i Accumulated within the adsorbent particle

The initial condition for the intraparticle phase mass balance is:

$$\bar{Y}_i(\bar{r}, \bar{t}_p = 0) \quad = \quad 0 \tag{IV-6}$$

The boundary conditions for the intraparticle phase mass balance are:

$$\frac{\partial \bar{Y}_i(\bar{r} = 0, \bar{t}_p)}{\partial \bar{r}} \quad = \quad 0 \tag{IV-7}$$

$$\frac{\partial}{\partial \bar{t}_p} \int_0^1 \bar{Y}_i(\bar{r}, \bar{t}_p) \, \bar{r}^2 d\bar{r} \quad = \quad Bi_{c,i} \left[\bar{C}_i(\bar{t}_p) - \bar{C}_{p,i}(\bar{r}=1, \bar{t}_p) \right] \tag{IV-8}$$

For multicomponent mixtures, the nonlinear equation which couples Equations IV-2 through IV-8 is the IAST equation. Luft (1984) found that the IAST equation described competition for multicomponent mixtures. The IAST equation written in terms of i components and in dimensionless variables is:

$$\bar{C}_{p,i}(\bar{r}, \bar{t}_p) \quad = \quad \frac{\bar{Y}_i(\bar{r}, \bar{t}_p) Y_{e,i} - \dfrac{\varepsilon_p}{\rho_a} \bar{C}_{p,i}(\bar{r}, \bar{t}_p) C_{o,i}}{C_{o,i} \displaystyle\sum_{j=1}^{m} \left[\bar{Y}_j(\bar{r}, \bar{t}_p) Y_{e,j} - \dfrac{\varepsilon_p}{\rho_a} \bar{C}_{p,j}(\bar{r}, \bar{t}_p) C_{o,j} \right]} \cdot \left[\frac{\displaystyle\sum_{k=1}^{m} \left[n_k [\bar{Y}_k(\bar{r}, \bar{t}_p) Y_{e,k} - \dfrac{\varepsilon_p}{\rho_a} \bar{C}_{p,j}(\bar{r}, \bar{t}_p) C_{o,i}] \right]}{n_i K_i} \right]^{n_i} \tag{IV-9}$$

For single-solutes, the Freundlich isotherm was used to relate the liquid-phase concentration at the exterior of the adsorbent to the adsorbent phase concentration.

Equations IV-2 through IV-9 contain two independent dimensionless variables: time, $\bar{t}_s$, and radial position, $\bar{r}$, and three dependent variables: liquid phase concentration, $\bar{C}_i,(t_s)$, the solid phase concentration, $\bar{q}_i(r,t_s)$, and the liquid phase concentration at the exterior and interior of the adsorbent $\bar{C}_p(r,t_s)$. These equations were solved by Friedman (1984) and his computer algorithms were used to determine the surface diffusivities.

D. Dimensionless Groups Which Describe the Multicomponent BPSDM

The solutions to the BPSDM are characterized by the following dimensionless groups and are being investigated, since they have an impact on the design and operation of the DCBR:

$$Dg_{s,i} = \frac{\rho_a q_{e,i}(1-\varepsilon)}{\varepsilon C_{o,i}} = \frac{M q_{e,i}}{\varepsilon V C_{o,i}} \qquad \text{(IV-10)}$$

$$Dg_{p,i} = \frac{\varepsilon_p(1-\varepsilon)}{\varepsilon} = \frac{M\varepsilon_p}{\varepsilon\rho_a V} \qquad \text{(IV-11)}$$

$$Dg_i = Dg_{s,i} + Dg_{p,i} \qquad \text{(IV-12)}$$

$$Bi_{c,i} = \frac{k_{f,i}\, R\, (1-\varepsilon)}{(D_{s,i}\, Dg_i + D_{p,i}\, Dg_{p,i})\varepsilon} \qquad \text{(IV-13)}$$

$$X_i = \frac{D_{s,i}\, Dg_i}{D_{s,i}\, Dg_i + D_{p,i}\, Dg_{p,i}} \qquad \text{(IV-14)}$$

$$Z_i = \frac{Dg_{p,i}(D_{p,i} - D_{s,i})}{D_{s,i}\, Dg_i + D_{p,i}\, Dg_{p,i}} \qquad \text{(IV-15)}$$

The surface solute distribution parameter, $Dg_{s,i}$, is defined in Section III-D. The pore solute distribution parameter, $Dg_{p,i}$, is the mass of adsorbate i in the adsorbent pores divided by the mass of adsorbate i in the liquid-phase under equilibrium conditions. This dimensionless group will be the same for all solutes in a given system, since it is a function of the porosity of the reactor, ε, and the adsorbent void fraction, ε_p.

The total adsorbent equilibrium capacity, Dg_i, is the sum of the surface solute distribution parameter, $Dg_{s,i}$, and the pore solute distribution parameter, $Dg_{p,i}$. As shown in Equation IV-12, it is based on the single solute capacity evaluated at the initial concentration of the batch reactor.

The Biot number, $Bi_{c,i}$, includes a combined surface and pore diffusivity. It compares the liquid-phase mass transfer rate to the total intraparticle phase mass transfer rate. A combined Biot number greater than 30 would insure an intraparticle controlled process and would insure a good determination of the surface diffusivity.

The dimensionless group, X_i, is the ratio of the rate of pore diffusion to the combined rate of pore and surface diffusion. The dimensionless group, Z_i, has no physical meaning.

The conversion to dimensionless variables reduces the number of independent parameters to seven dimensionless groups: $1/n_i$, $Dg_{s,i}$, $Dg_{p,i}$, Dg_i, $Bi_{c,i}$, X_i, and Z_i. Of the seven dimensionless groups, only the six dimensionless groups act independently: $1/n_i$, $Dg_{s,i}$, $Dg_{p,i}$, $Bi_{c,i}$, X_i, and Z_i.

V. PRELIMINARY CALCULATIONS AND CRITERIA NEEDED TO CONDUCT A SUCCESSFUL DIFFERENTIAL COLUMN BATCH REACTOR STUDY

It is important to minimize the effect of the liquid-phase mass transfer resistance in the differential column batch reactor (DCBR) such that the surface diffusivity can be estimated accurately. Presented below are the preliminary calculations and criteria needed to conduct a successful differential column batch reactor study.

A. Representative Sample from the Batch Reactor

The hydraulic retention time, τ_r, is an important consideration in the design of the DCBR. It is defined as the time needed to circulate one reactor volume of water through the reactor and is related to the rate at which water is passed through the differential carbon column. If the hydraulic retention time is low enough, then there will be no concentration gradient across the differential carbon bed (See Section V-E for more discussion). The hydraulic retention time is calculated by the following equation:

$$\tau_r = \frac{V}{Q} \qquad \text{(V-1)}$$

where V is the volume of the reactor, and Q is the volumetric flow rate through the packed column. The hydraulic retention time is only a qualitative criteria and can not be used to quantitatively select the proper flow rate and velocity through the column.

The liquid-phase samples which are collected during a DCBR experiment are used to determine the concentration history profile for a given solute. However, the total sample volume removed should not be more than 5% of the reactor volume.

B. Obtaining a Representative Carbon Sample

The carbon dosage, D_o, is another important design consideration, because a representative sample of the carbon must be taken. A large dosage of activated carbon was used such that the isotherm capacity observed in the DCBR would be the same as the capacity observed in the isotherm experiment. It was assumed that at least 80 particles were a representative sample of the carbon. The equilibrium capacities that were obtained from the batch rate studies were similar to the capacities obtained from the isotherm studies; consequently, a large enough carbon dosage was selected to give the same equilibrium capacity as the isotherm experiments. See Section VI-B for further discussion.

C. Temperature Dependence of Equilibrium and Kinetic Parameters

The differential column batch reactor was conducted at the same temperature as the isotherm study, because both equilibrium and diffusion rate are temperature dependent.

Since a high flow rate may cause heating of the water from the pump, the the temperature inside the reactor was monitored. However, the temperature inside the reactor was the same as the laboratory. Consequently, no additional cooling of the DCBR was required.

D. Effect of the Liquid-Phase Mass Transfer Rate

For Biot numbers greater than 30, it was found that surface diffusion was required to explain the rate of uptake for the VOCS and the contribution of pore diffusion was determined to be negligible. Therefore, the Biot number which was based on the surface was used to determine the effect of the liquid-phase mass transfer resistance. See Section III-D for further discussion. The Biot number, which is based on the surface diffusivity of a given adsorbent, is defined by Equation III-10.

The film transfer coefficient correlation, which was reported by Wakao et. al., 1978, was used in the DCBR calculations, because the Reynolds numbers in differential column batch reactor studies were high and this correlation was developed for higher Reynolds numbers:

$$k_{f,i} = \frac{D_{1,i}}{2\,R}\left[\,2 + 1.1\,N_{Re}^{\;0.6}\,N_{Sc,i}^{\;1/3}\right] \qquad (V\text{-}3)$$

in which, $D_{1,i}$ is the liquid diffusivity of the adsorbate in water; N_{Re} is the Reynolds number; and $N_{Sc,i}$ is the Schmidt number for a given adsorbate. These dimensionless groups were defined by the following equations:

$$N_{Re} = \frac{2\,R\,\rho_1\,v_i\,\varepsilon}{\mu} \qquad (V\text{-}4)$$

$$N_{Sc,i} = \frac{\mu}{\rho_1\,D_{1,i}} \qquad (V\text{-}5)$$

in which, v_i is the interstitial velocity, ε is the void fraction of the carbon bed, μ is the viscosity of water, and ρ_1 is the density of water. The liquid diffusivity of the adsorbate in water, $D_{1,i}$ was calculated using the following equation (Hayduk and Laudie, 1974):

$$D_{1,i} = \frac{13.25\;10^{-5}}{\mu^{1.14}\;\;V_b^{\,.589}} \qquad (V\text{-}6)$$

E. Calculation of the Concentration Gradient Across the Differential Carbon Column

The final requirement of the DCBR is that the influent and effluent concentration across the differential carbon column are approximately the same. The mechanisms, which are important in transporting the solute across the bed, are advection and axial dispersion. A plug flow, fixed-bed model was used to calculate the ratio of the effluent liquid-phase concentration leaving the differential carbon column to the influent liquid-phase concentration entering the differential carbon carbon, C_{eff}/C_{inf}, because if axial dispersion was included, then a higher C_{eff}/C_{inf} would be determined. Therefore, a design which is based a plug flow model would be more conservative. The assumptions that are built into the following model (Friedman, 1984) are: 1) there is no axial dispersion in the fixed-bed, 2) the surface concentration is zero, and 3) the system is operating at steady state. The final form of the equation is:

$$C_{eff}/C_{inf} = e^{-3St_i} \tag{V-7}$$

The Stanton number, St_i, is defined as:

$$St_i = k_{f,i}(1 - \varepsilon)\tau/R(\varepsilon) \tag{V-8}$$

in which, τ is the packed bed contact time and is equal to the ratio of the volume of the carbon bed to the volumetric flow rate through the carbon bed.

Equation V-7 can also be used to describe the concentration gradient in a DCBR. Although Equation V-7 was developed for the steady-state operation of a fixed-bed adsorber with a constant influent concentration, it can be used to estimate the required flow rate in a DCBR. In a DCBR, the liquid-phase concentration decreases with time and the surface concentration increases with time; consequently, the actual concentration gradient across the column for the DCBR would be less than the concentration gradient which would be calculated using Equation V-7. Therefore, the use of Equation V-7 to estimate the proper flow rate would be conservative.

The ratio of C_{eff}/C_{inf} that was greater than or equal to 0.95 was chosen as that required to guarantee no concentration gradient across the DCBR. This would require a Stanton number less than or equal to 0.017.

When the concentration gradient across the differential carbon column is greater than or equal to 0.95, and the Stanton number is less than or equal to 0.017, the concentration across the differential column is the same as the concentration in the DCBR reservoir.

The Stanton number is the ratio of the rate of mass transfer due to film transfer to the rate of mass transfer due to advection. If the Stanton number is greater than 0.017, then it is necessary to increase the hydraulic loading or decrease the hydraulic retention time such that the the Stanton number will be less than 0.017. For a given flow rate or hydraulic retention time, the column diameter can be reduced such that the film transfer coefficient and the Stanton number would increase.

VI. COMPARISON OF THE MATHEMATICAL MODELS USED TO SIMULATE THE DIFFERENTIAL COLUMN BATCH REACTOR

Surface diffusivities of various VOCS were determined by comparing batch rate data to a mathematical model. Three models were used for this comparison. They were: (a) the batch homogeneous surface diffusion model (BHSDM) which includes liquid-phase mass transfer and surface diffusion, (b) batch pore surface diffusion model (BPSDM) which includes liquid-phase mass transfer and surface and pore diffusion, and (c) the pore diffusion model (BPDM) which includes liquid-phase mass transfer and pore diffusion. The developments of the BHSDM and BPSDM were presented in Sections III and IV, respectively. The BPDM may be derived from the BPSDM by setting the surface flux equal to zero.

Presented below are the experimental results and analyses for the determination of the intraparticle diffusion coefficients using the models described above.

A. Single Solute Batch Rate Results

Seven single-solute rate studies were conducted on two granular activated carbons in Milli-Q water with four volatile organic compounds. The four compounds were the weakly-adsorbing cis-1,2 dichloroethene, the moderately-adsorbing trichloroethene, and the strongly-adsorbing tetrachloroethene and toluene. Appendix 6 contains the experimental data and the physical characteristics of the system. Table VI-1 contains the single solute Freundlich isotherm parameters for the components used in the models.

The BHSDM and BPSDM were the two models which were used to simulate the single-solute concentration history profiles in the batch rate study. Figures VI-1 through VI-6 contain the experimental data for trichloroethene, tetrachloroethene, cis-1,2 dichloroethene, and toluene along with the BHSDM

Table VI-1. Single Solute Freundlich Isotherm Constants Used in the BHSDM and BPSDM Calculations

Compound	Concentration Range (µm/L)	Water Matrix Carbon Type	Temperature Equilibration Time, Days pH (°C)	Best Fit Freundlich K (95% C.I.) $(\mu m/g)(L/\mu m)^{1/n}$	Best Fit Freundlich 1/n (95% C.I.) (Dimensionless)	References
cis-1,2 dichloroethene	.117-42.6	Milli-Q F-400 (200x400)	13.8 28 7.5-8.0	46.9 (46.2 - 47.6)	.5562 (.5509-.5618)	Kato (1985) •
Ethylbenzene	.042-26.6	Milli-Q F-400 (200x400)	13.8 21 7.5-8.0	714.3 (682.0-746.0)	.2953 (.2759-.3147)	Kato (1985)
Tetrachloroethene	.021-7.05	Milli-Q F-400 (200x400)	9.0-11.0 6.0 6.0	650.6 (530.1-798.9)	.4579 (.4365-.4794)	Luft (1984) •
Tetrachloroethene	.161-15.7	Milli-Q F-400 (200x400)	13.8 33 7.5-8.0	435.0 (426.0-444.0)	.3850 (.3721-3973)	Kato (1985)
Toluene	.056-37.5	Milli-Q F-400 (200x400)	13.8 25 7.5-8.0	475.0 (467.0-483.0)	.3282 (.3212-.3351)	Kato (1985) •
Trichloroethene	.043-2.73	Milli-Q F-400 (200x400)	9.0-11.0 6.5 6.0	196.6 (124.4-310.6)	.4163 (.3620-.4706)	Luft (1984) •
Trichloroethene	.04-9.13	Milli-Q WV-G (200x400)	9.0-11.0 6.5 6.0	181.0 (148.7-220.3)	.4073 (.3850-.4295)	Luft (1984) •
Trichloroethene	.114-23.6	Milli-Q F-400 (200x400)	13.8 31 7.5-8.0	192.0 (187.0-197.0)	.4328 (.4195-.4462)	Kato (1985)
M-Xylene	.363-35.7	Milli-Q F-400 (200x400)	13.8 21 7.5-8.0	1044.0 (997.0-1110.0)	.2458 (.2237-.2679)	Kato (1985)
O-Xylene	.363-35.7	Milli-Q F-400 (200x400)	13.8 26 7.5-8.0	895.0 (851.0-938.0)	.2587 (.2369-.2806)	Kato (1985)

• Used in the BHSDM, BPSDM, and BPDM calculations

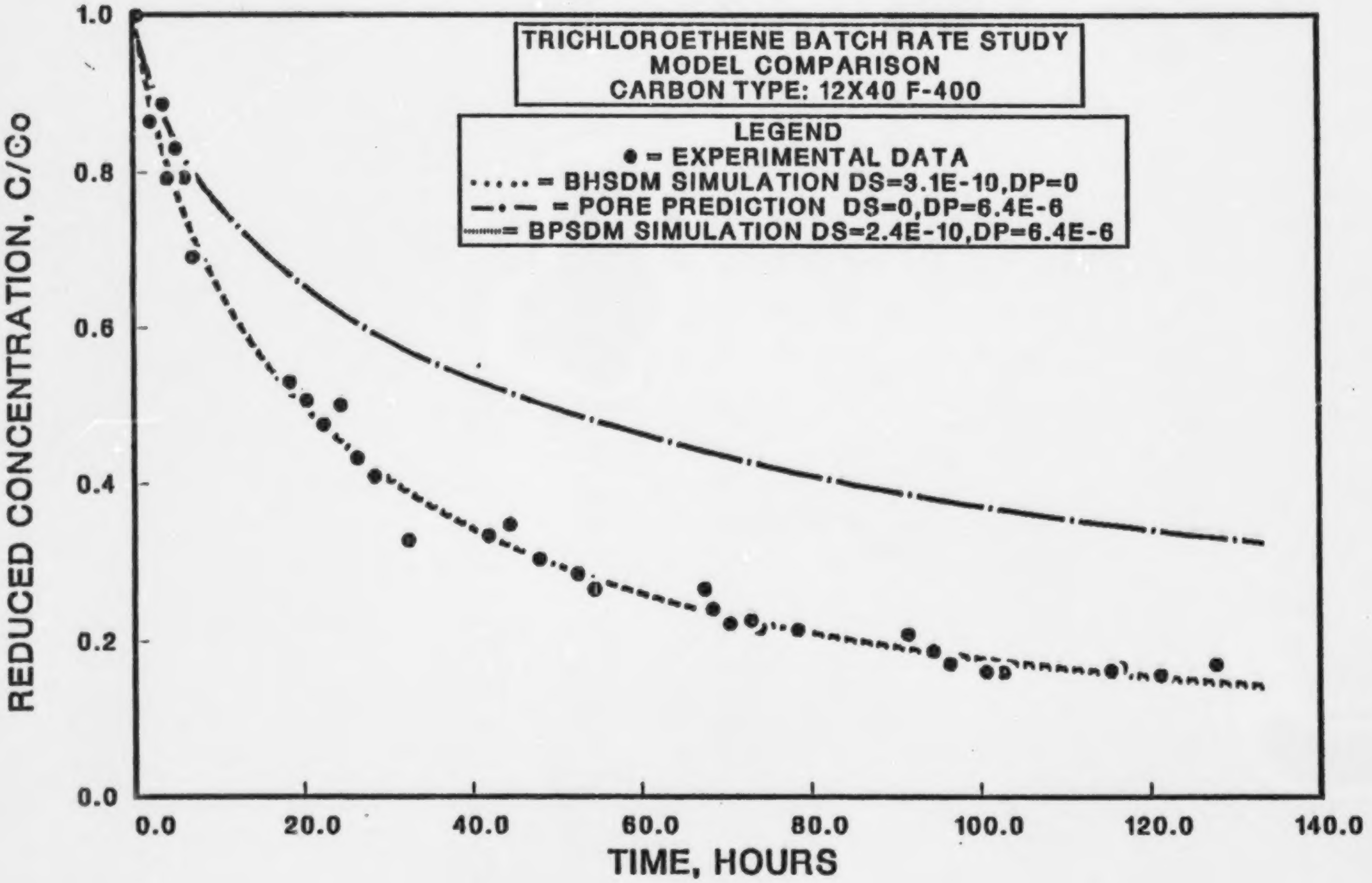

Figure VI-1. BHSDM and BPSDM Simulations for Trichloroethene in Milli-Q Water and (12x40) F-400 Carbon (C_o = 1322.7 μg/L).

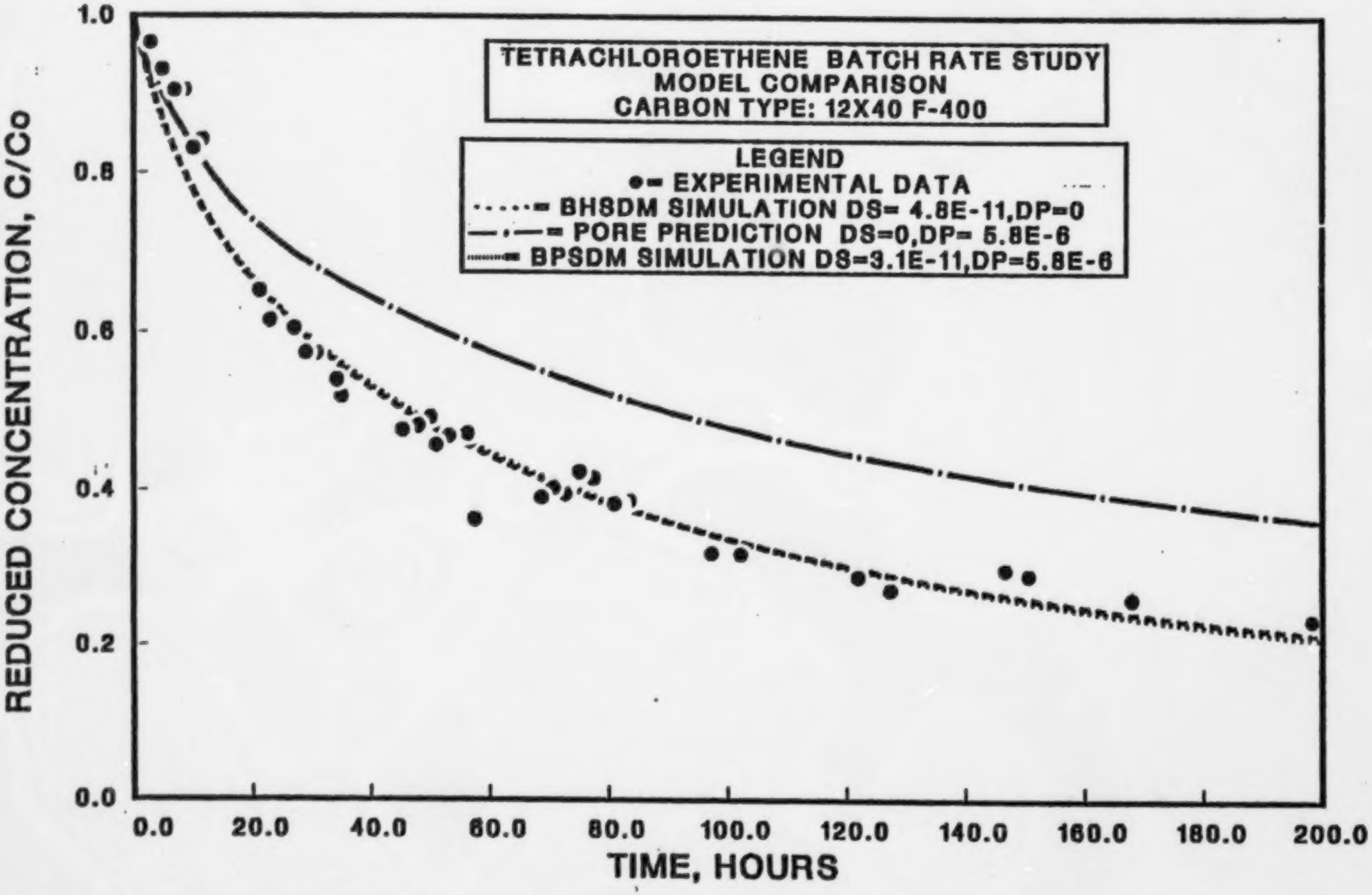

Figure VI-2. BHSDM and BPSDM Simulations for Tetrachloroethene in Milli-Q Water and (12x40) F-400 Carbon C_o = 1438.4 μg/L).

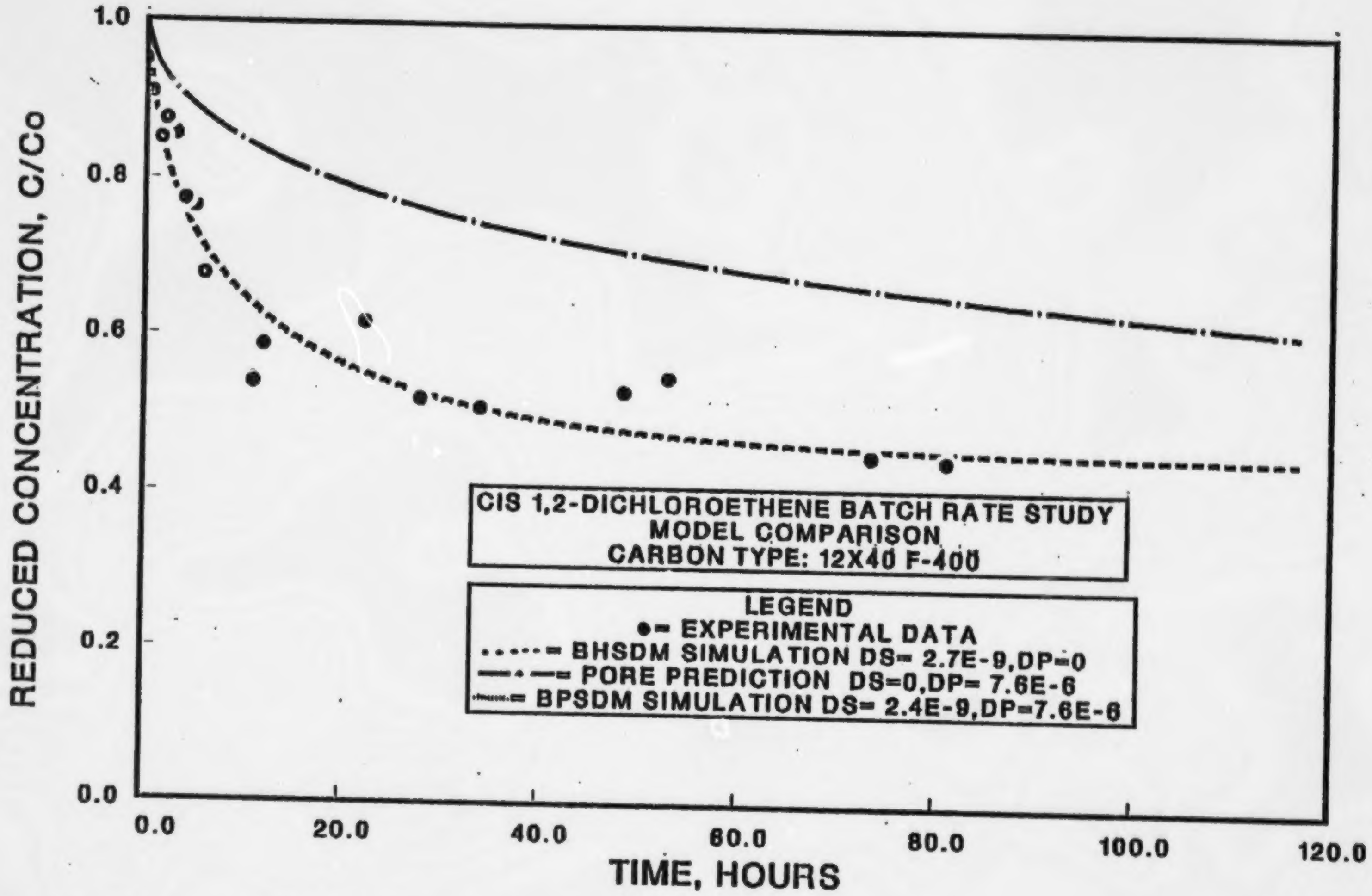

Figure VI-3. BHSDM and BPSDM Simulations for cis-1,2 dichloroethene in Milli-Q Water and (12x40) F-400 Carbon (C_o = 507.0 μg/L).

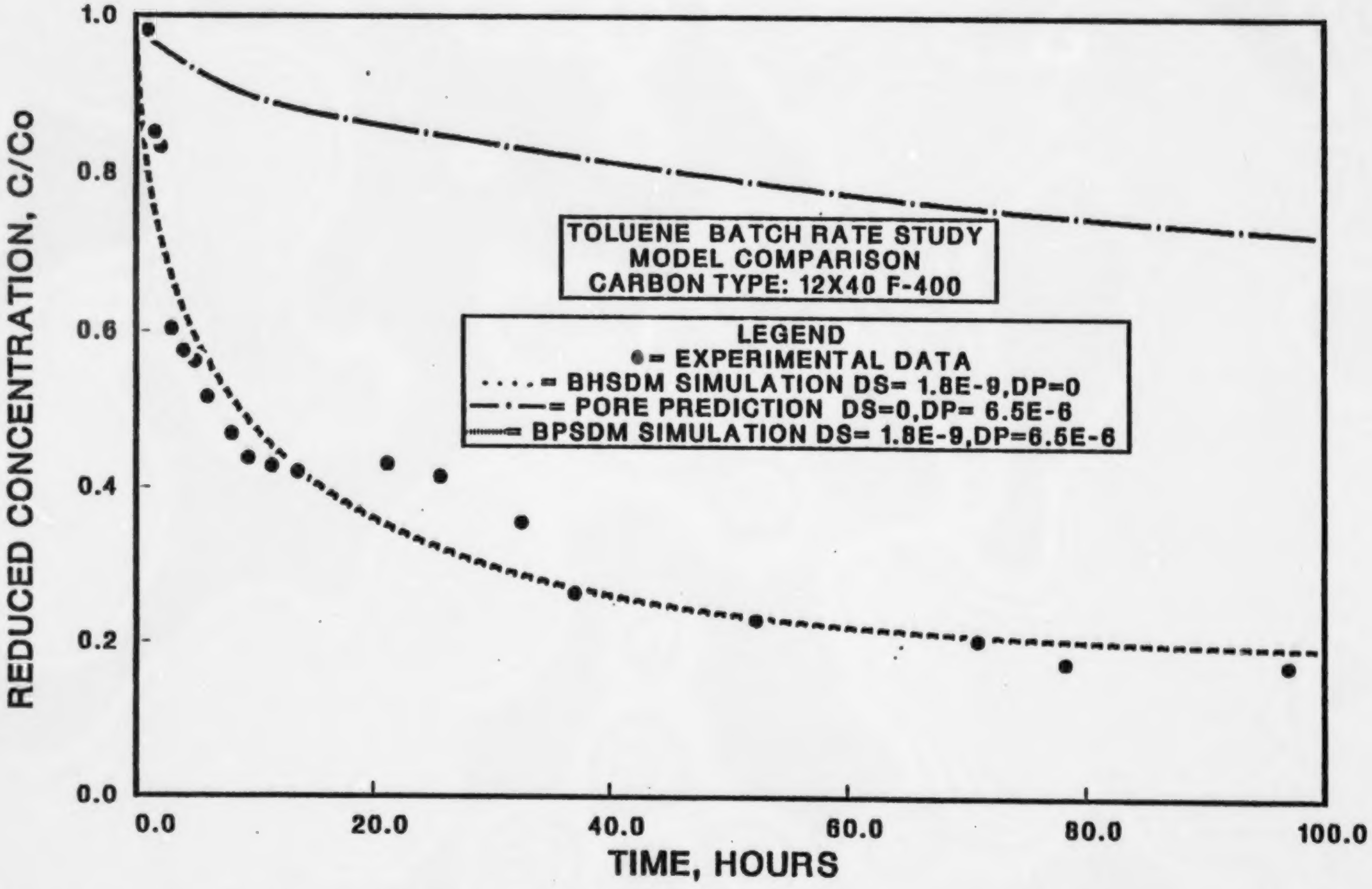

Figure VI-4, BHSDM and BPSDM Simulations for Toluene in Milli-Q Water and (12x40) F-400 Carbon (C_o = 372.4 μg/L).

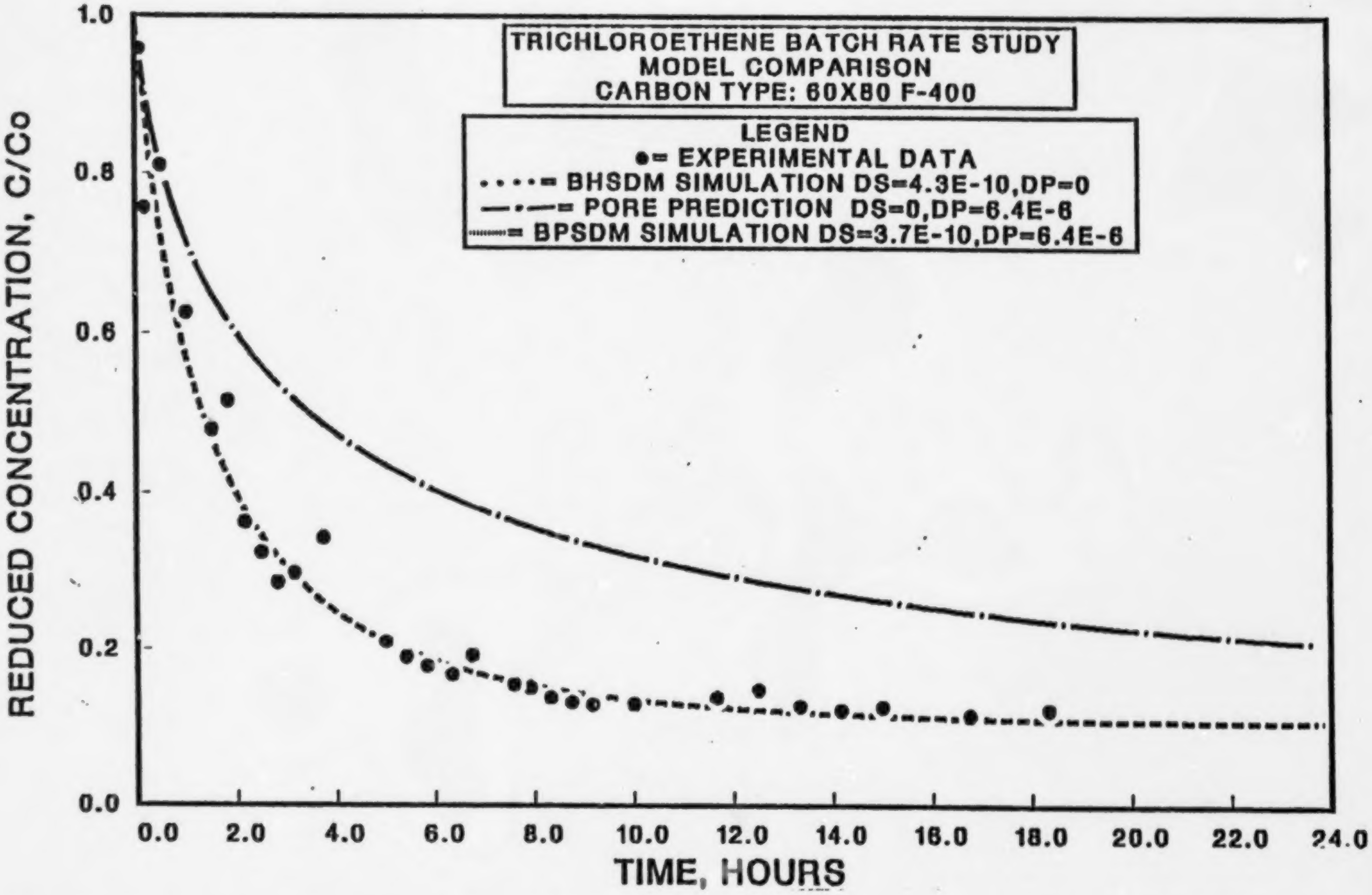

Figure VI-5. BHSDM and BPSDM Simulations for Trichloroethene in Milli-Q Water and (60x80) F-400 Carbon (C_o = 1329.8 μg/L).

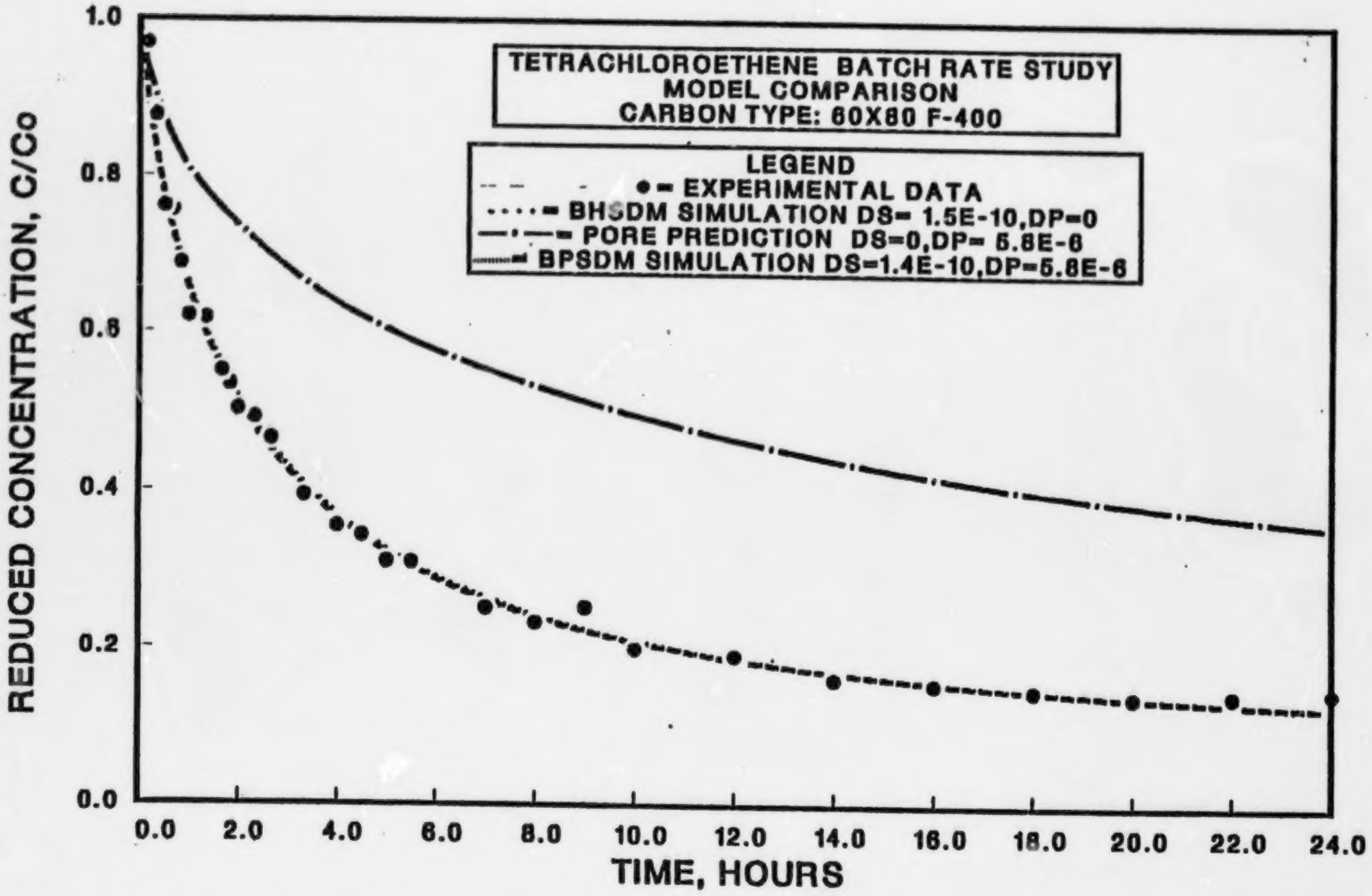

Figure VI-6. BHSDM and BPSDM Simulations for Tetrachloroethene in Milli-Q Water and (60x80) F-400 Carbon (C_o = 1504.0 μg/l).

and BPSDM simulations and a BPDM prediction. The best fit of the film transfer coefficient, $k_{f,i}$, and the surface diffusivity, $D_{s,i}$, were determined by a two parameter search using the BHSDM. The best fit was determined by minimizing the sum of the differences between measured and calculated concentrations using the following equation:

$$S(\min) = \sum_i \left[(C_i\text{data} - C_i\text{model})^2 / (C_i\text{data})^2 \right]^{1/2} \qquad \text{(VI-1)}$$

in which S(min) represents the minimum relative error between the model calculated values and the data.

The 95% confidence intervals for k_f and D_s were calculated for the two parameters using the equation presented by Draper and Smith (1981).

$$S(\theta) = S(\min) \left[1 + \frac{p}{n-p} F(p, n-p, 1-\alpha) \right]^{1/2} \qquad \text{(VI-2)}$$

in which, $S(\theta)$ is the relative error for a given confidence contour; p is the number of parameters; (n − p) is the number of degrees of freedom; n is the number of data points; α is the desired confidence contour and F is the distribution function based on the number of degrees of freedom, the number of data points, and the desired confidence limit.

Table VI-2 contains the 95% confidence intervals for $k_{f,i}$ and $D_{s,i}$, the Biot numbers which were based on the surface diffusivity and the Stanton numbers.

For the pore and surface model diffusion simulations, the pore diffusivity, $D_{p,i}$, was a calculated value and did not add an additional unknown to the system. The best fit $k_{f,i}$ from the BHSDM and the calculated

Table VI-2. Surface Diffusivities and Film Transfer Coefficients Determined by Fitting Experimental Data Using the HSDM and the HPSDM

Compound	Initial Concentration (μg/L)	Water Matrix Carbon Type	Temperature (°C)	Best Fit Surface Diffusivity Using HPSDM $D_s x10^{10}$ (cm^2/s)	Best Fit Surface Diffusivity Using HSDM (95% C.I.) $D_s x10^{10}$ (cm^2/s)	Best Fit Film Transfer Coefficient Using HSDM (95% C.I.) $K_f x10^3$ (cm/s)	Biot Number (Dimensionless)	Stanton Number
cis-1,2 dichloroethene	507.0	Milli-Q F-400 (12x40)	13.0	24.0	27.0 (17.0-51.0)	7.10 (.85-100.0)	28.72	0.0266
Tetrachloroethene	1438.4	Milli-Q F-400 (12x40)	11.0	0.31	0.48 (0.35-0.65)	7.10 (4.3-100.0)	46.81	0.0302
Tetrachloroethene	1504.0	Milli-Q F-400 (60x80)	11.0	1.35	1.50 (1.25-1.80)	43.0 (32.5-90.0)	19.07	0.0382
Toluene	372.4	Milli-Q F-400 (12x40)	23.0	27.9	18.0 (15.0-22.5)	700.0 (—)	133.50	0.0134
Trichloroethene	1322.7	Milli-Q F-400 (12x40)	11.0	2.45	3.10 (2.5-3.8)	4.51 (2.8-10.0)	18.14	0.0316
Trichloroethene	1241.5	Wausau WV-G (12x40)	11.0	1.90	2.80 (2.4-3.2)	15.4 (—)	82.08	0.0077
Trichloroethene	1329.8	Milli-Q F-400 (60x80)	11.0	3.70	4.30 (3.0-6.5)	14.0 (0.90-8.50)	8.37	0.029
Trichloroethene	1441.6	Wausau F-400 (12x40)	11.0	1.85	2.60 (2.35-2.95)	15.00 (—)	75.82	0.0085
Trichloroethene	1318.6	Milli-Q WV-G (12x40)	11.0	2.50	3.30 (2.5-4.7)	3.10 (—)	14.5	0.0205

$D_{p,i}$ were held constant while a search was done on the surface diffusivity using the BPSDM. The porosity of the adsorbent, ε_p, was accounted for in the development of the BPSDM and the true pore diffusion coefficient incorporated both the porosity and tortuosity of the adsorbent. See equation IV-1. The following equation was used to determine the pore diffusivity:

$$D_{p,i} = \frac{D_{l,i}}{\tau_p} \qquad \text{(VI-3)}$$

in which, τ_p is the tortuosity. It was set equal to 1.0, because it will give the largest contribution of pore diffusion flux. $D_{l,i}$ is the liquid diffusivity of adsorbate i which was calculated from Equation V-6.

As shown in Figures VI-1 to VI-6, the BHSDM and the BPSDM simulations produced nearly identical concentration profiles. In all cases, as shown in Table VI-2, the $D_{s,i}$ which was determined using the BPSDM was slightly lower than the $D_{s,i}$ which was determined in the BHSDM. The difference in the values of $D_{s,i}$ from the two models reflected the contribution of the pore flux. Therefore, the pore flux was negligible. This was further confirmed from the BPDM predictions. Since the tortuosity was set equal to one in these predictions, the largest flux due to the contribution of pore diffusion coefficient would be observed. However, as shown in Figures VI-1 to VI-6, the pore prediction did not predict any of the concentration profiles. Accordingly, it can be concluded that surface diffusion was the controlling mechanism. See Appendix 8 for a sample data file and a sample output file for both the BHSDM and BPSDM.

Two single-solute rate studies were conducted in Milli-Q water with F-400, 60x80 mesh carbon. The two compounds were the moderately-adsorbing trichloroethene and the strongly-adsorbing tetrachloroethene. As shown in Table VI-2, the $D_{s,i}$ which was determined using the BHSDM and BPSDM for the smaller carbon were larger than the $D_{s,i}$ measured for the larger carbon (12x40).

As discussed in Section V, the Biot and Stanton numbers may be used to evaluate whether the concentration difference across the DCBR is negligible and whether film transfer or surface diffusion controls the rate of adsorption. Table VI-2 displays the values of the Biot and Stanton numbers. Even though all of the Stanton numbers were not less than 0.017 (This would indicate that effluent to influent concentration ratio was less than 0.95.) the concentration gradient across the differential carbon column was not large. Also, it was not always possible to obtain Biot numbers greater than 30 (This would guarantee surface diffusion controlled.), because the carbon dosages which were required to guarantee a representative would cause the experiment to become film transfer limited. See Section V-B for further discussion. Eventually, larger batch reactors which contained similar carbon dosages were used to resolve this problem.

B. Equilibrium Time and Concentration for the Differential Column Batch Reactor Studies

The equilibrium time and concentration of the DCBR were determined in order to evaluate whether the capacity which was observed in the batch rate study agreed with the bottle point isotherm. That is, if the DCBR was run for a long length of time, the equilibrium concentrations would agree with the isotherm capacities that are reported in Table VI-3. Moreover, it was expected that the equilibration time would be longer for the larger carbon particles (12x40), while the equilibration time would be shorter for the smaller carbon particles (60x80). The equilibrium concentration was determined by solving Equation 5-2 in Appendix 5 by trial and error. The equilibration time was determined by running the BHSDM until 105% of the

Table VI-3. Comparison of the Model Equilibrium Times and Concentrations to the Final Observed Concentration and Times for the Differential Column Batch Reactor Studies

Compound	Initial Concentration (µg/L)	Water Matrix Carbon Type	Model Equilibrium Concentration (µg/L)	model Equilibrium Time Days	Final Observed Concentration in the DCBR (µg/L)	Final Observed Time in the DCBR Days
cis-1,2 dichloroethene	507.0	Milli-Q F-400 (12x40)	228.6	3.61	225.0	4.23
Tetrachloroethene	1438.4	Milli-Q F-400 (12x40)	54.9	39.04	338.2	8.26
Tetrachloroethene	1504.0	Milli-Q F-400 (60x80)	152.9	1.56	221.2	1.0
Toluene	372.4	Milli-Q F-400 (12x40)	69.3	4.00	64.0	3.67
Trichloroethene	1322.7	Milli-Q F-400 (12x40)	91.3	20.00	224.6	5.32
Trichloroethene	1241.5	Wausau WV-G (12x40)	75.1	20.49	208.4	5.11
Trichloroethene	1329.8	Milli-Q F-400 (60x80)	141.4	1.96	163.9	0.76
Trichloroethene	1441.6	Wausau F-400 (12x40)	92.3	22.22	237.8	5.89
Trichloroethene	1518.6	Milli-Q WV-G (12x40)	104.7	21.74	190.7	22.12

equilibrium concentration was attained. As shown in Table VI-3, the equilibrium concentration determined in the batch reactor appeared to be the same as the equilibrium concentration determined from the equilibrium data when the time to achieve equilibrium is considered. In other words, the equilibrium concentration was less then the final concentration of the DCBR when the model calculated equilibration time was greater than the time to achieve equilibrium was considered and the equilibrium concentration in the DCBR agreed with the equilibrium concentration if the DCBR study was run for an adequate length of time.

C. Multicomponent Results for the Wausau Water Matrix

1. Batch Rate Results Using Thawed Wausau Water Matrix

The purpose of this experiment was to determine the effect of the background material present in the Wausau water matrix on the adsorption rate of the carbon. Two batch rate studies which were conducted with F-400 and WV-G carbon used thawed Wausau water. This water was previously frozen so a minimum of biodegradation of the background material would occur and the concentration of trichloroethene was increased and used as a tracer to determine the competitive interactions of the background material other than the VOCS. An analysis of the Wausau water before and after freezing are shown in Table VI-4. As shown in Table IV-4, the concentration of the VOCS decreased and benzene appeared. Benzene was never found in the raw Wausau water matrix. However, if the raw Wausau water was aged, benzene was found; accordingly, it was thought that some of the aromatic compounds degraded to form benzene in the presence of the background Wausau water matrix.

The DCBR data for trichloroethene which was conducted in organic-free-water and in thawed Wausau water matrix are displayed in Figures VI-7 and VI-8

Table VI-4. Biological, Organic, and Inorganic Analysis of Wausau Well #4 Water Matrix Collected on February 20, 1984

Compound	Raw Water Analysis (3/15/84) (µg/L)	Thawed Water Analysis (8/23/84) (µg/L)
cis-1,2 dichloroethene	213.2	86.4
Trichloroethene	193.5	6.4
Tetrachloroethene	128.8	55.4
Benzene	N.A.	56.9
Toluene	59.1	24.4
Ethylbenzene	N.A.	2.4
o,p-Xylene	29.5	11.7
m-Xylene	20.8	3.6

N.A. Not Analyzed
Samples were analyzed using a Hewlett-Packard 5830A Purge and Trap Gas chromatograph

Component	Result
Total Organic Carbon (TOC)	8.4 mg/L
TOC after Purging	8.6 mg/L
Total Carbon (TC)	29.2 mg/L
TC after Purging	22.3 mg/L
Manganese	1.27 mg/L
Iron	5.3 mg/L
Fluoride	0.34 mg/L
Alkalinity	84.0 mg/L
pH	6.8
Color	64.0
Ames Test	Negative
Standard Plate Count	Negative

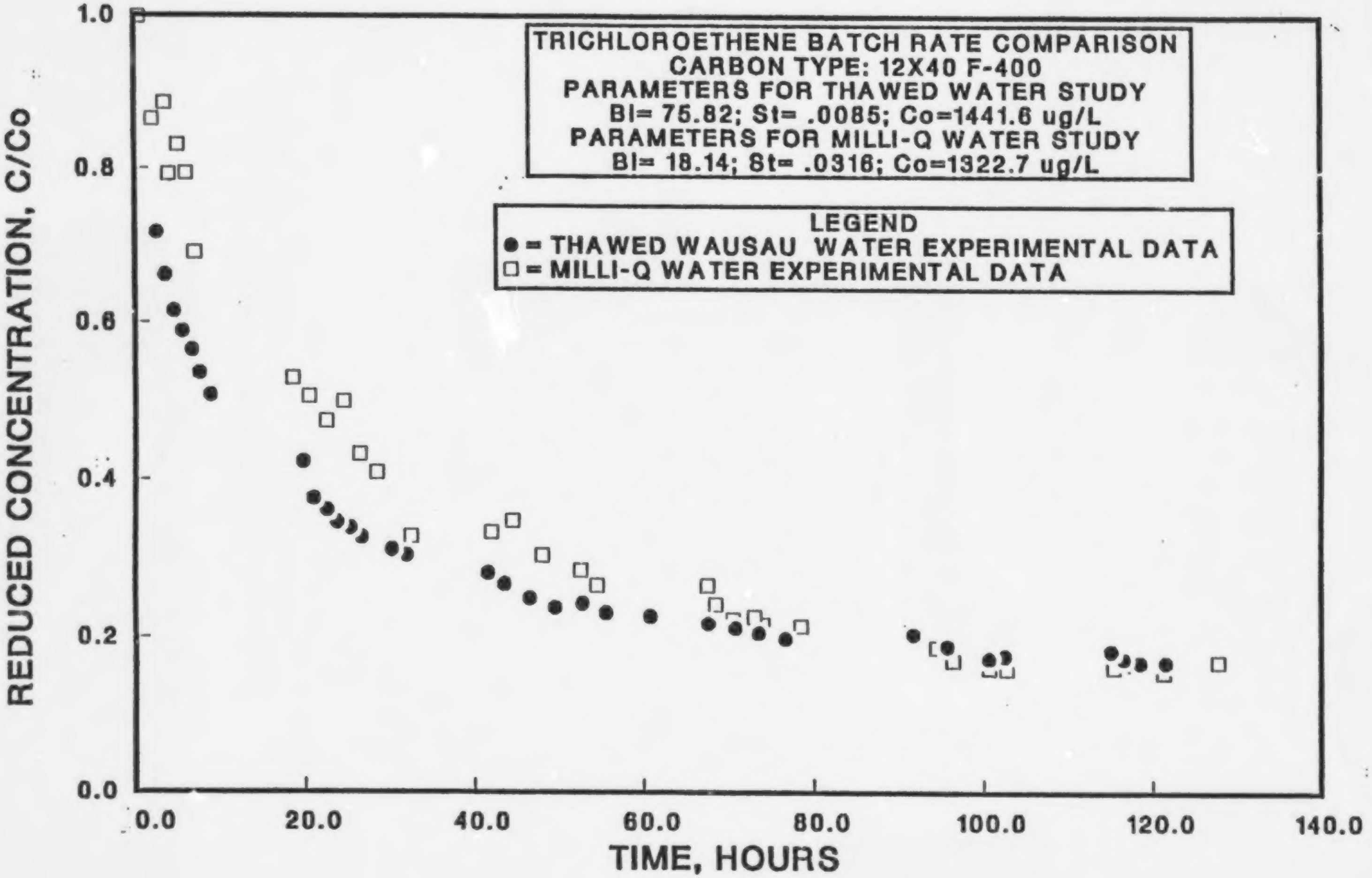

Figure VI-7. Comparison of the Trichloroethene Batch Rate Data Collected in Milli-Q Water and Thawed Wausau Water on F-400 Carbon (D_s for Trichloroethene in Thawed Wausau Water: 2.6 10^{-10}cm^2/s; D_s for Trichloroethene in Milli-Q Water: 3.1 10^{-10} cm^2/s).

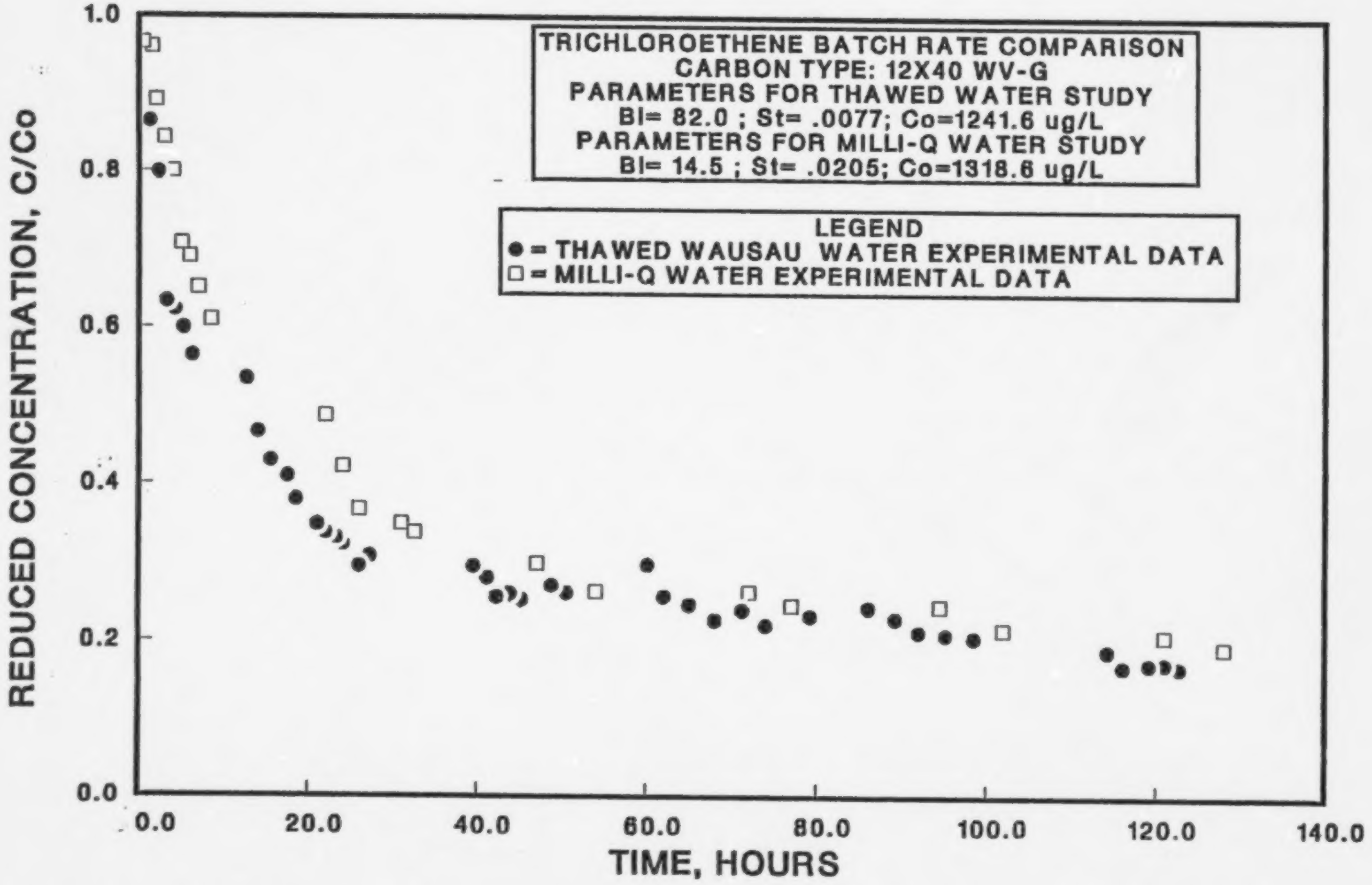

Figure VI-8. Comparison of the Trichloroethene Batch Rate Data Collected in Milli-Q Water and Thawed Wausau Water on WV-G Carbon (D_s for Trichloroethene in Thawed Wausau Water: 2.8 $10^{-10}$$cm^2$/s; D_s for Trichloroethene in Milli-Q Water: 3.3 10^{-10} cm^2/s).

for F-400 and WV-G carbons, respectively. The organic-free-water trichloroethene data showed a slower approach to equilibrium than the trichloroethene data which was collected in the thawed Wausau water matrix, because it was conducted at a higher flow rate. However, the difference between the organic-free-water results and the thawed Wausau water results was due to the difference in the liquid-phase mass transfer rate. As shown in Table VI-2, the surface diffusion coefficients for the trichloroethene in the organic-free-water were within the experimental error of those which were determined in thawed Wausau water. Since most of the VOCS were lost when the Wausau water was frozen, the background total organic carbon in the thawed Wausau water had little effect on the adsorption rate and capacity for the solute trichloroethene when its concentration was increased to approximately 1400 μg/L.

2. Multicomponent Results Using Fresh Wausau Water Matrix

The purpose of this experiment was to determine if a multicomponent batch rate study would provide useful kinetic data on the components which were found in the Wausau water matrix and whether the correlation presented in Section VIII-B would allow the concentration history profiles to be predicted using the the BPSDM. Appendix 7 contains the raw data along with the operational parameters.

The rate study was conducted for only four days, because the pump failed. Only five data points were collected over the four day period and the problems with the degradation of the aromatic compounds (See Section VI-C-3) made it impossible to predict the data with the BPSDM or to use it to determine the surface diffusivities. In addition, the selection of a proper carbon dosage was not possible for the determination of the surface diffusivities. If a high carbon dosage was chosen to observe the concentration history profile of the weakly-adsorbing solute, it would result in a film transfer limited case for the strongly-adsorbing solute. If a low carbon dosage was chosen to observe the concentration history profile of the strongly-adsorbing solute, the concentration history profile for the weakly-adsorbing solute would not be significantly depressed enough to see a concentration profile and allow the determination of the intraparticle surface diffusion coefficient. The model prediction, using the calculated surface diffusivities from equation VIII-13, along with the raw data are displayed in Table 7-3.

3. Degradation Results of the Wausau Water Matrix

The purpose of this experiment was to determine if a 0.22μm Millipore filter would eliminate microorganisms in the Wausau water well that may have been responsible for the degradation of the aromatic compounds. The other objective was to determine if the 0.22μm filter would adsorb any of the volatile organic compounds found in the water matrix.

a. Experimental Plan for Degradation Experiments

(1) A 40 liter glass carboy was filled with water from Wausau well #4. The water was spiked with toluene to an initial concentration of 64 μg/L. The glass carboy was placed in a constant temperature environment of 11°C. A magnetic stirrer was used to keep the contents of the carboy well mixed.

(2) A pump and a 0.22μm filter were placed in series. Sampling ports were placed before and after the filter. Five liters of the spiked water was initially flushed through the system to purge the lines.

(3) Samples were taken before and after the 0.22μm filter. Two

samples were taken immediately after purging the lines: an influent to the filter and an effluent to the filter. This would determine whether any of the compounds present in the water matrix were adsorbed onto the filter. Eight influent and effluent samples were then collected during the first hour of the experiment in 45 ml sample vials. The eight filtered and unfiltered samples were stored in an isothermal environment of 11°C.

(4) A filtered and unfiltered sample was then analyzed using the purge and trap method for an eight day period. Table VI-5 contains the raw data.

b. Results

Figure VI-9 shows the data for the degradation experiment. The compounds of interest were trichloroethene, tetrachloroethene, cis-1,2 dichloroethene, and the spiked toluene. The influent and effluent concentrations of the immediate samples showed that no solutes adsorbed onto the 0.22µm filter. The eight day study resulted in the same influent and effluent concentrations for the cis-1,2 dichloroethene, trichloroethene, and tetrachloroethene. However, both the influent and effluent concentration for toluene showed that degradation was present. The 0.22µm filter will remove any known organism that could cause degradation. Also, toluene in organic-free-water showed no sign of degradation over a three week period when used as a standard for the purge and trap analysis. Therefore, toluene in the Wausau water matrix was degraded by some other mechanism.

Table VI-5. Degradation Study of the Wausau Water Matrix

Day	Influent (concentration, μg/L)	Effluent	Influent (concentration, μg/L)	Effluent	Influent (concentration, μg/L)	Effluent	Influent (concentration, μg/L)	Effluent
	cis-1,2 dichloroethene		Trichloroethene		Tetrachloroethene		Toluene	
0	74.0	70.0	52.0	49.0	36.0	38.0	64.0	62.0
2	74.0	76.0	52.0	55.0	38.0	36.0	54.0	62.0
3	74.0	72.0	50.0	48.0	36.0	32.0	43.0	42.0
4	76.0	71.0	54.0	48.0	38.0	31.0	37.0	49.0
5	72.0	68.0	48.0	48.0	34.0	33.0	22.0	24.0
6	68.0	68.0	42.0	42.0	29.0	29.0	—	—
8	74.0	62.0	50.0	45.0	32.0	26.0	19.0	22.0

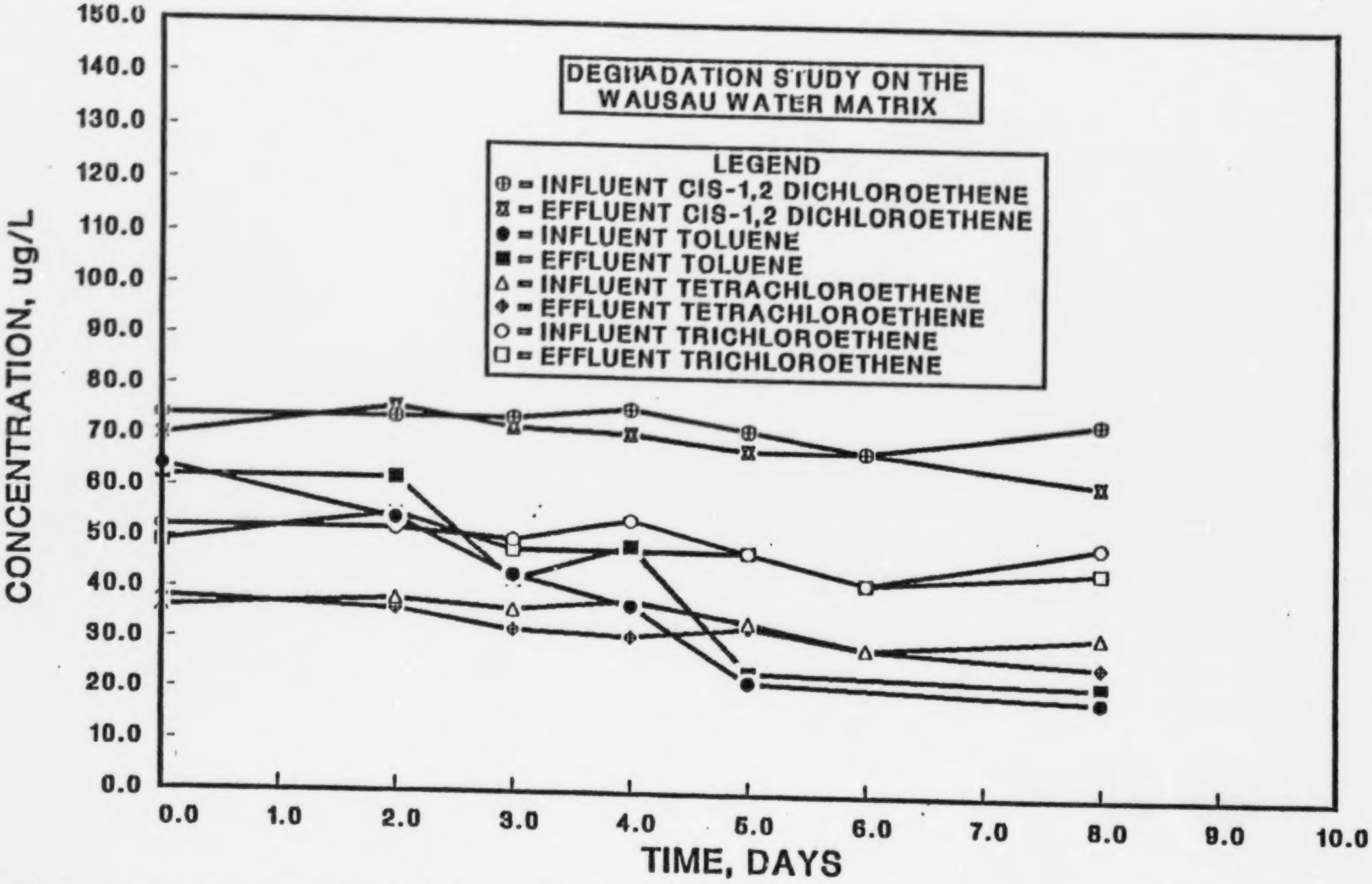

Figure VI-9. Results of the Degradation Study on the Fresh Wausau Water Matrix.

VII. SENSITIVITY ANALYSIS OF THE MODEL PARAMETERS WHICH CHARACTERIZE THE SOLUTIONS TO THE DIFFERENTIAL COLUMN BATCH REACTOR

In order to assess the impact of the model parameters on the determination of the surface diffusivity, a sensitivity analysis was conducted on all the parameters which affected the BHSDM calculations. These were the isotherm and kinetic parameters. The Freundlich isotherm parameters, K and 1/n, were determined independently and were assumed to be correct within experimental accuracy. Accordingly, the Freundlich parameters, K and 1/n, were varied plus or minus their 95% confidence interval in the sensitivity analysis. The film transfer coefficient and the surface diffusion coefficient were varied plus or minus 50% in the sensitivity analysis.

There are three important parameters to consider in the determination of the surface diffusivity which were illustrated by the sensitivity analysis: the Biot number and the Freundlich isotherm parameters K and 1/n. A high Biot number is desirable (Hand et. al. ; 1984), because the intraparticle mass transfer rate will control the adsorption rate and a good estimate of the surface diffusivity may be determined.

A. Sensitivity Analysis of the Liquid Phase Mass Transfer Rate and the Intraparticle Diffusion Rate in the Determination of the Surface Diffusion Rate

The impact of the film transfer coefficient and the surface diffusion coefficient on the DCBR study depends on the Biot number. The Biot numbers which were observed in the DCBR experiments ranged from 18.1 to 133.5. See Table VI-2. A sensitivity analysis, therefore, was conducted on Biot numbers of 18.1, 28.7, 75.8, and 133.5.

As the Biot number increases, it was expected that the effects of the film transfer rate would be reduced. Figures VII-1 to VII-8 display the effect of the film transfer coefficient and the surface diffusivity on the

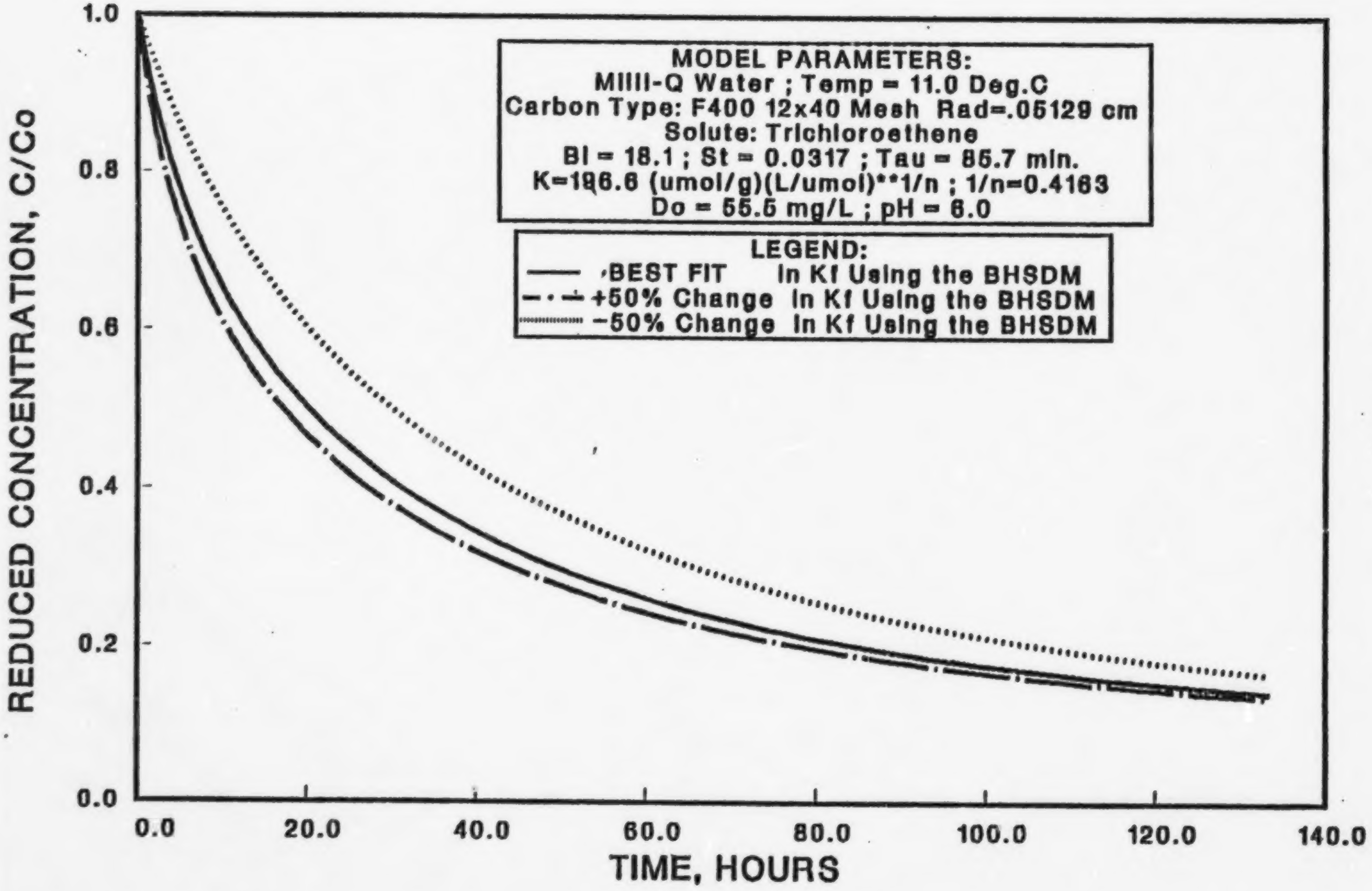

Figure VII-1. BHSDM Sensitivity Analysis of +/- 50% k_f for Trichloroethene in Milli-Q Water and (12x40) F-400 Carbon (Bi = 18.1; C_o = 1322.7 µg/L.

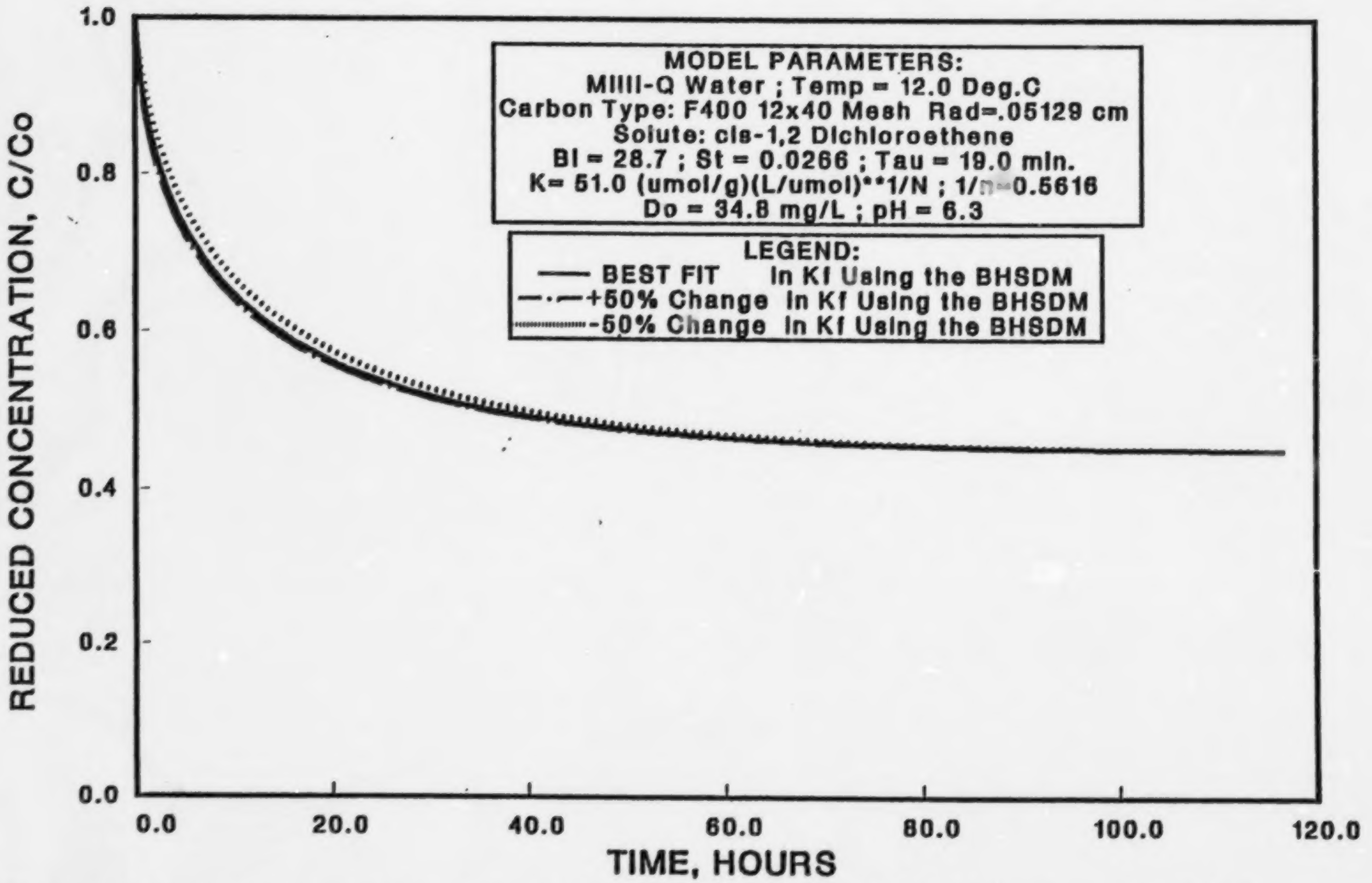

Figure VII-2. BHSDM Sensitivity Analysis of.+/- 50 k_f for cis-1,2 dichloroethene in Milli-Q Water and (12x40) F-400 Carbon (Bi=28.7 ; C_o = 507.0 μg/L)

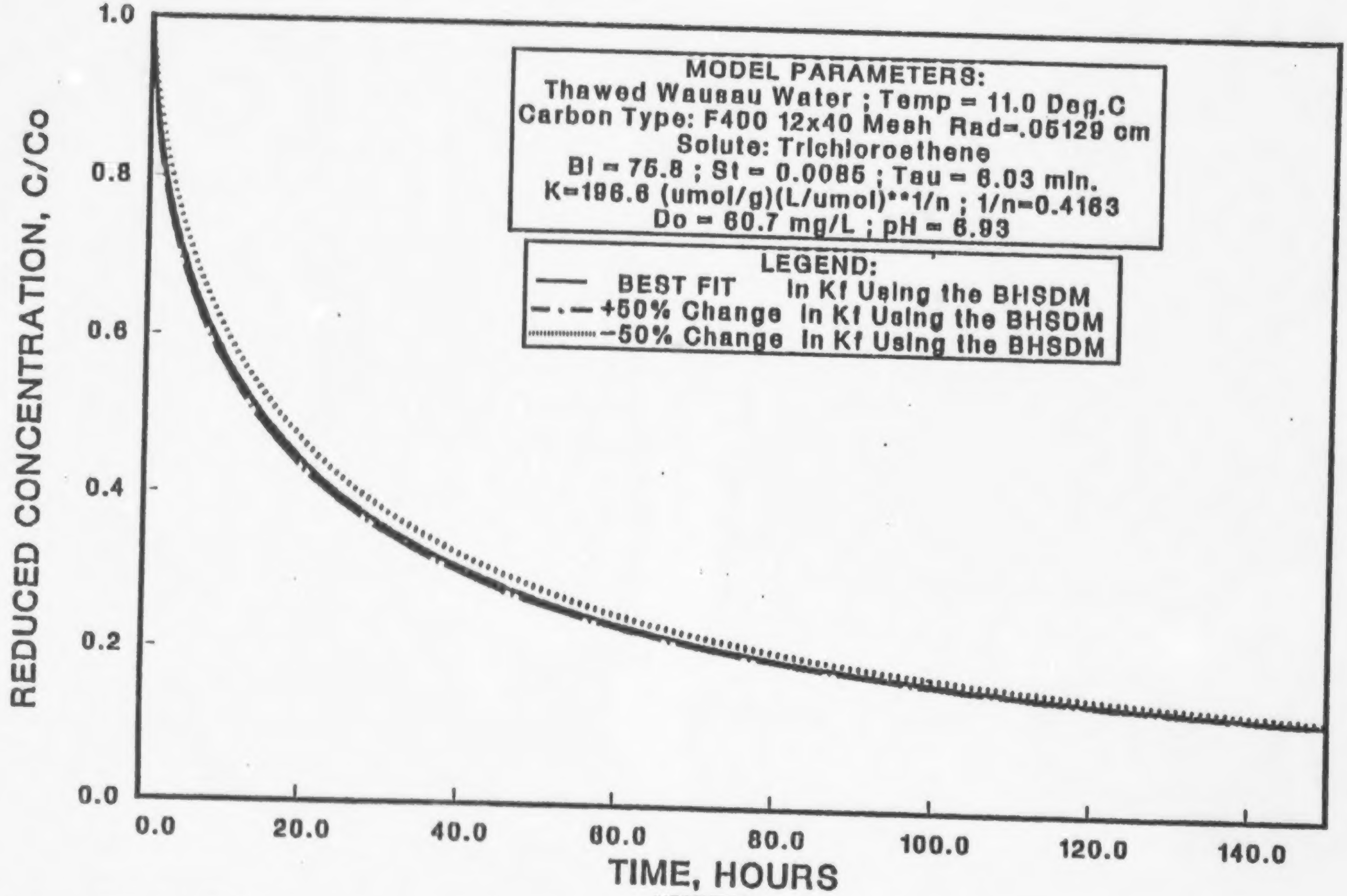

Figure VII-3. BHSDM Sensitivity Analysis of +/- 50% k_f for Trichloroethene in Thawed Wausau Water and (12x40) F-400 Carbon (Bi=75.8 ; C_o = 1441.6 µg/L).

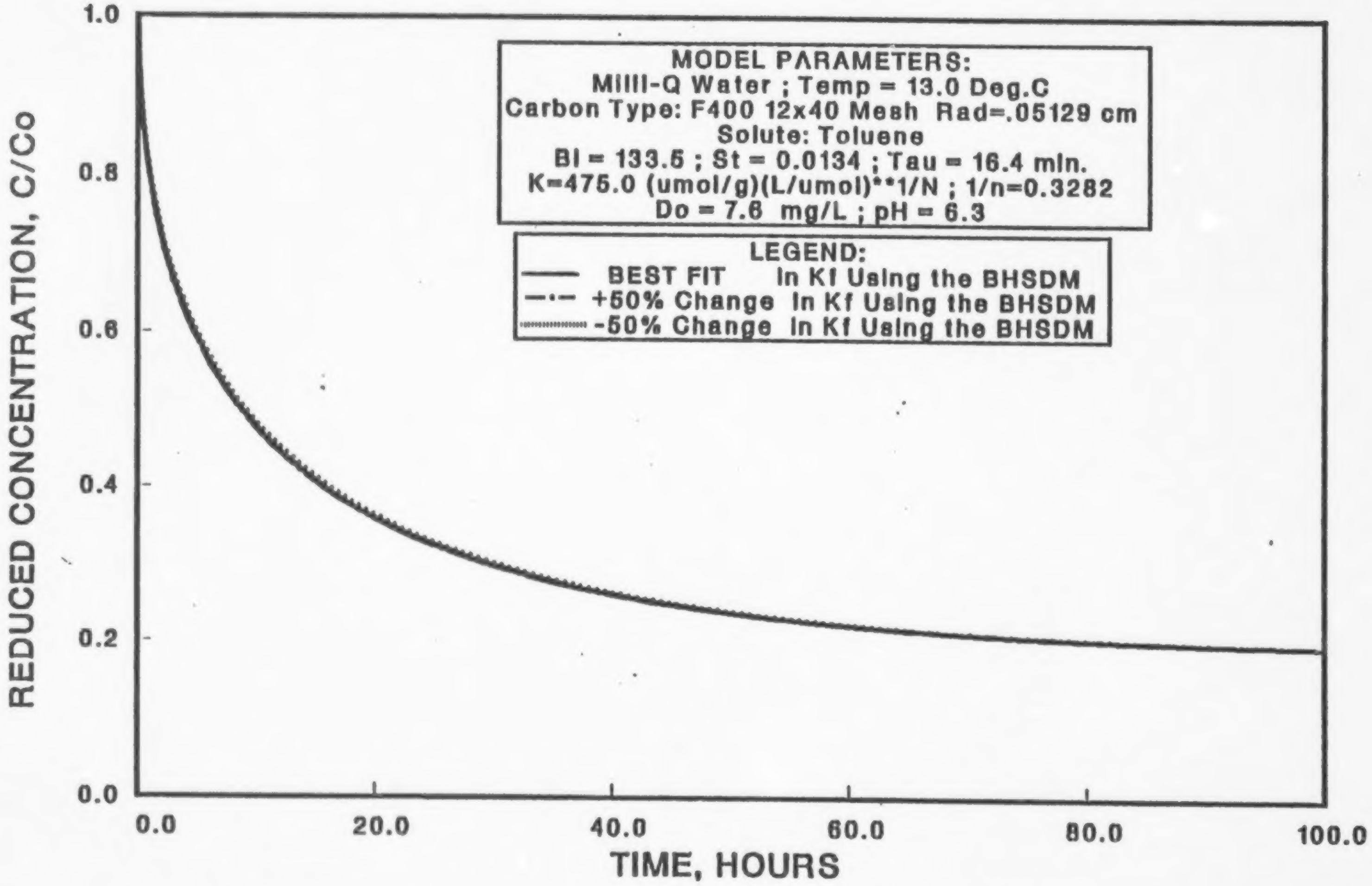

Figure VII-4. BHSDM Sensitivity Analysis of +/- 50% k_f for Toluene in Milli-Q Water and (12x40) F-400 Carbon (Bi = 133.5 ; C_o = 372.4 μg/L).

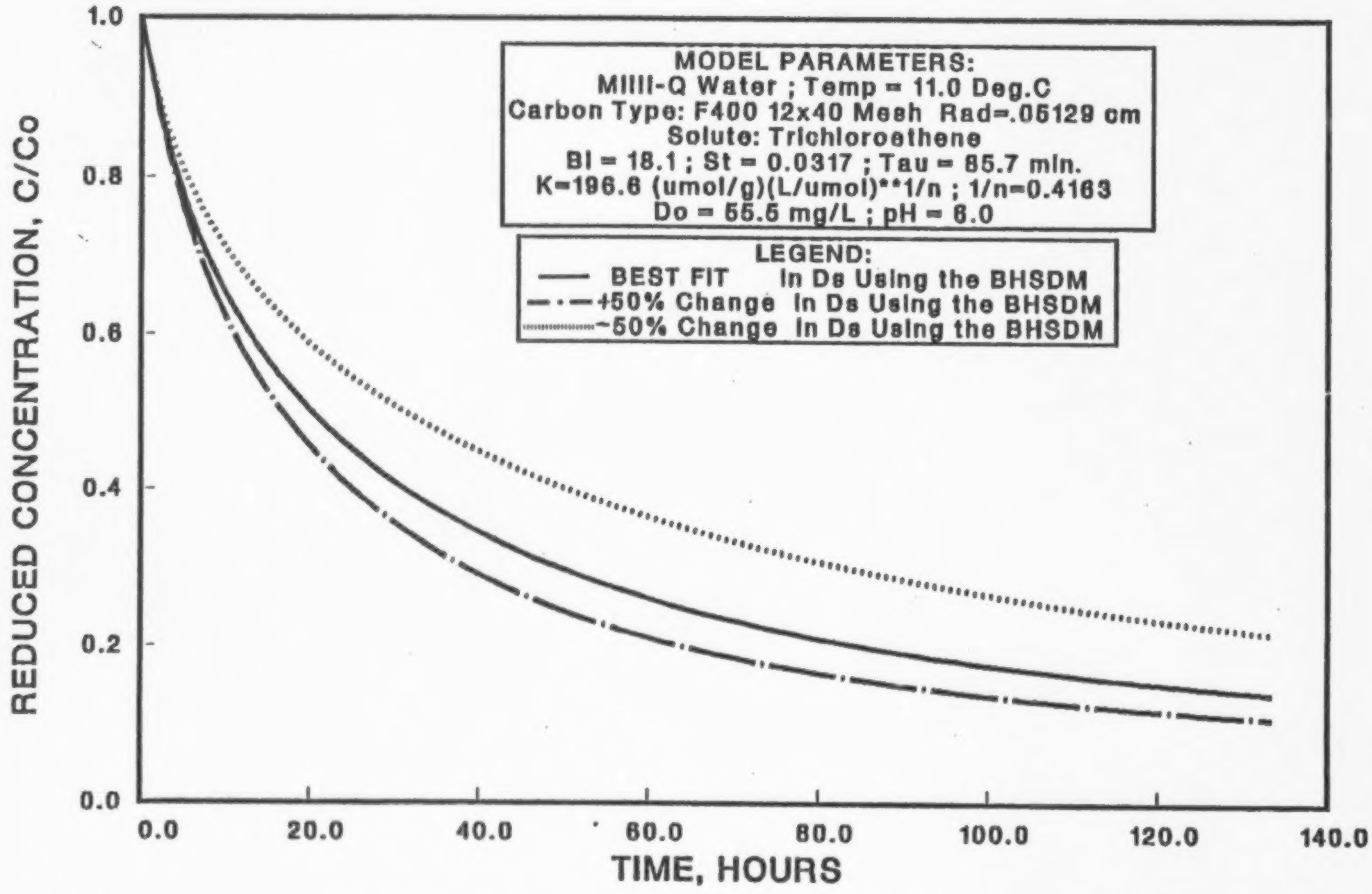

Figure VII-5. BHSDM Sensitivity Analysis of +/- 50% D_s for Trichloroethene in Milli-Q Water and (12x40) F-400 Carbon (Bi = 18.1; C_o = 1322.7 µg/L.

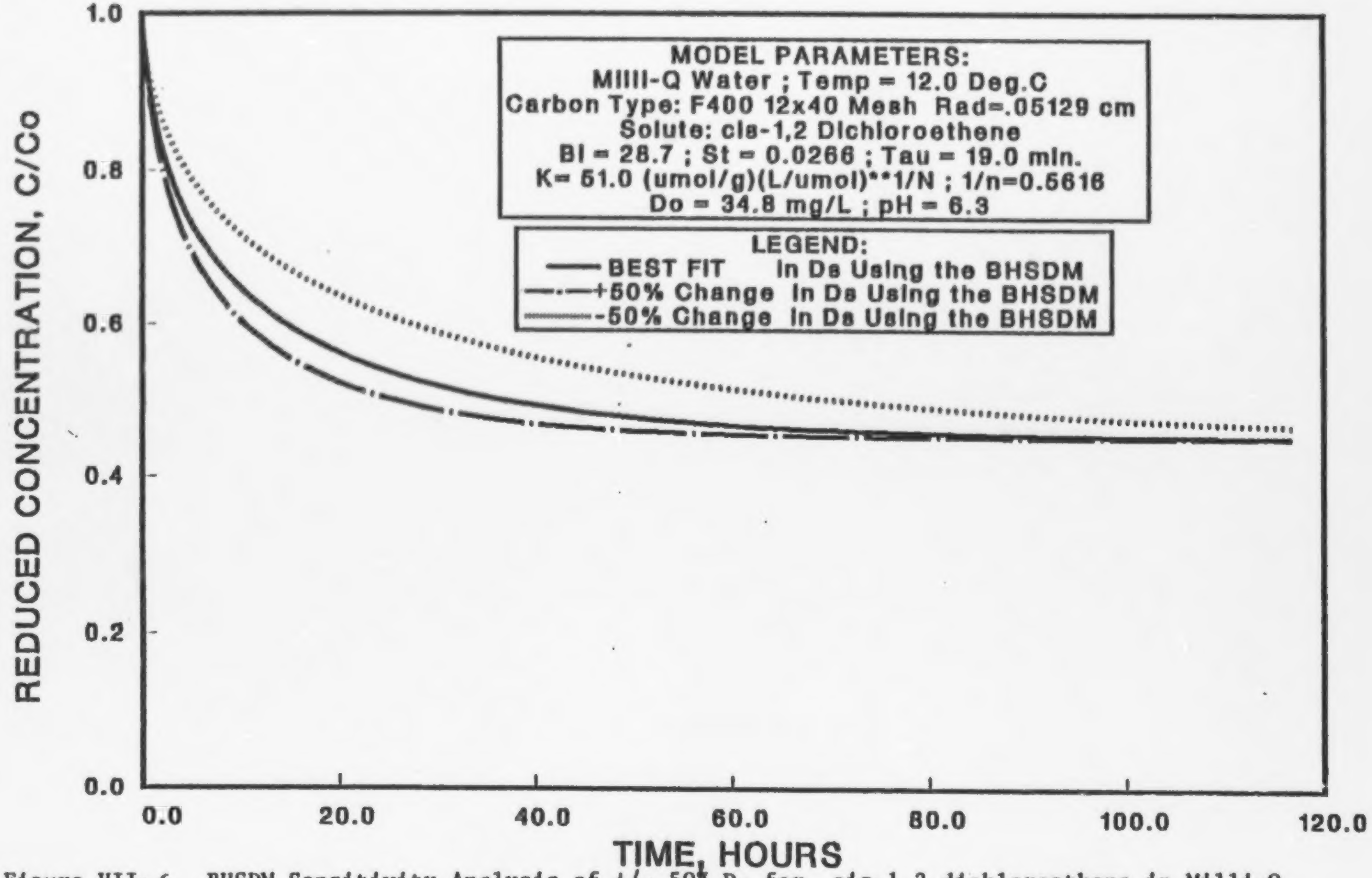

Figure VII-6. BHSDM Sensitivity Analysis of +/- 50% D_s for cis-1,2 dichloroethene in Milli-Q Water and (12x40) Carbon (Bi=28.7 ; C_o = 507.0 µg/L).

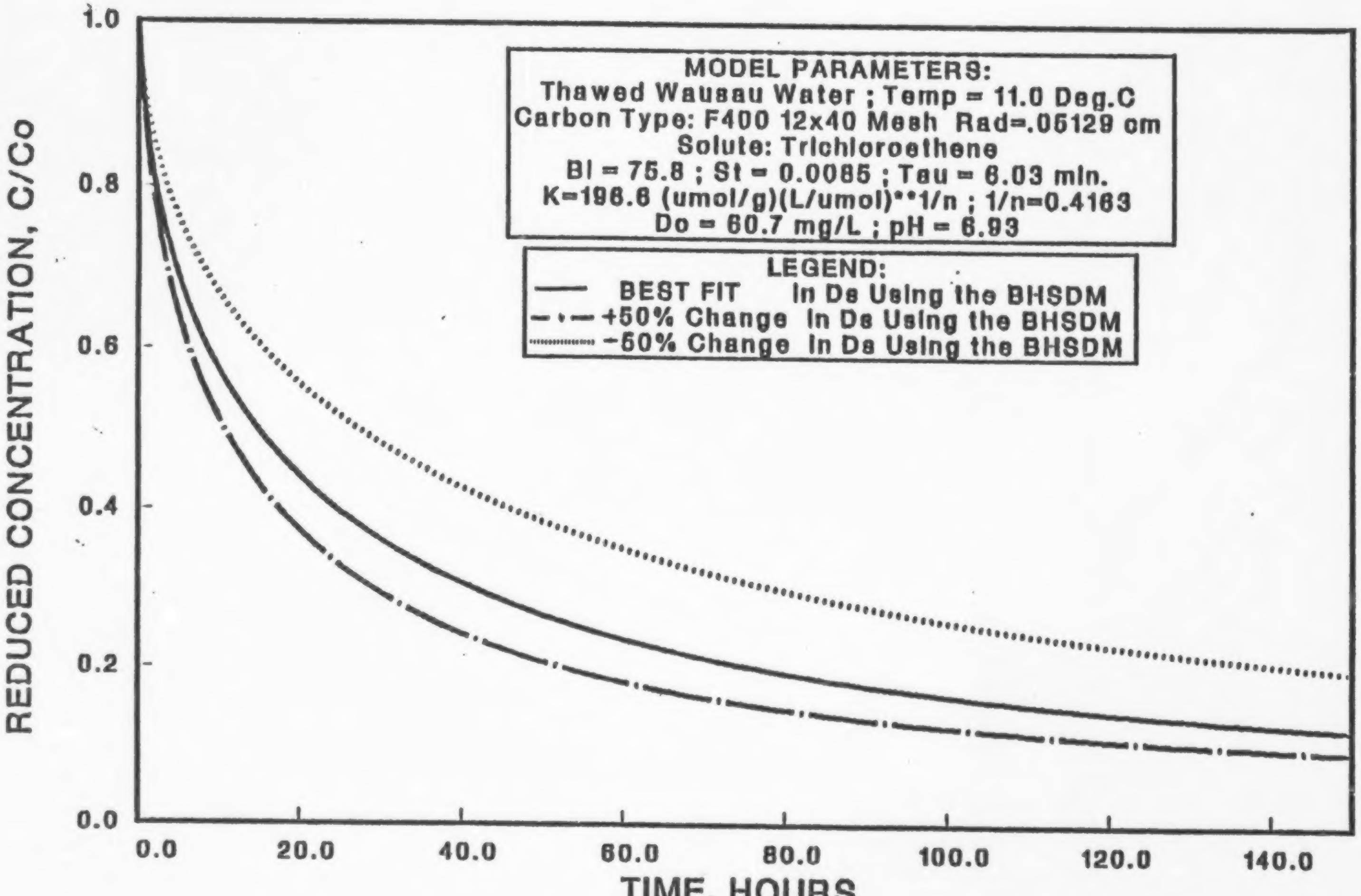

Figure VII-7. BHSDM Sensitivity Analysis of +/- 50% D_s for Trichloroethene in Thawed Wausau Water and (12x40) F-400 Carbon (Bi = 75.8 ; C_o = 1441.6 µg/L).

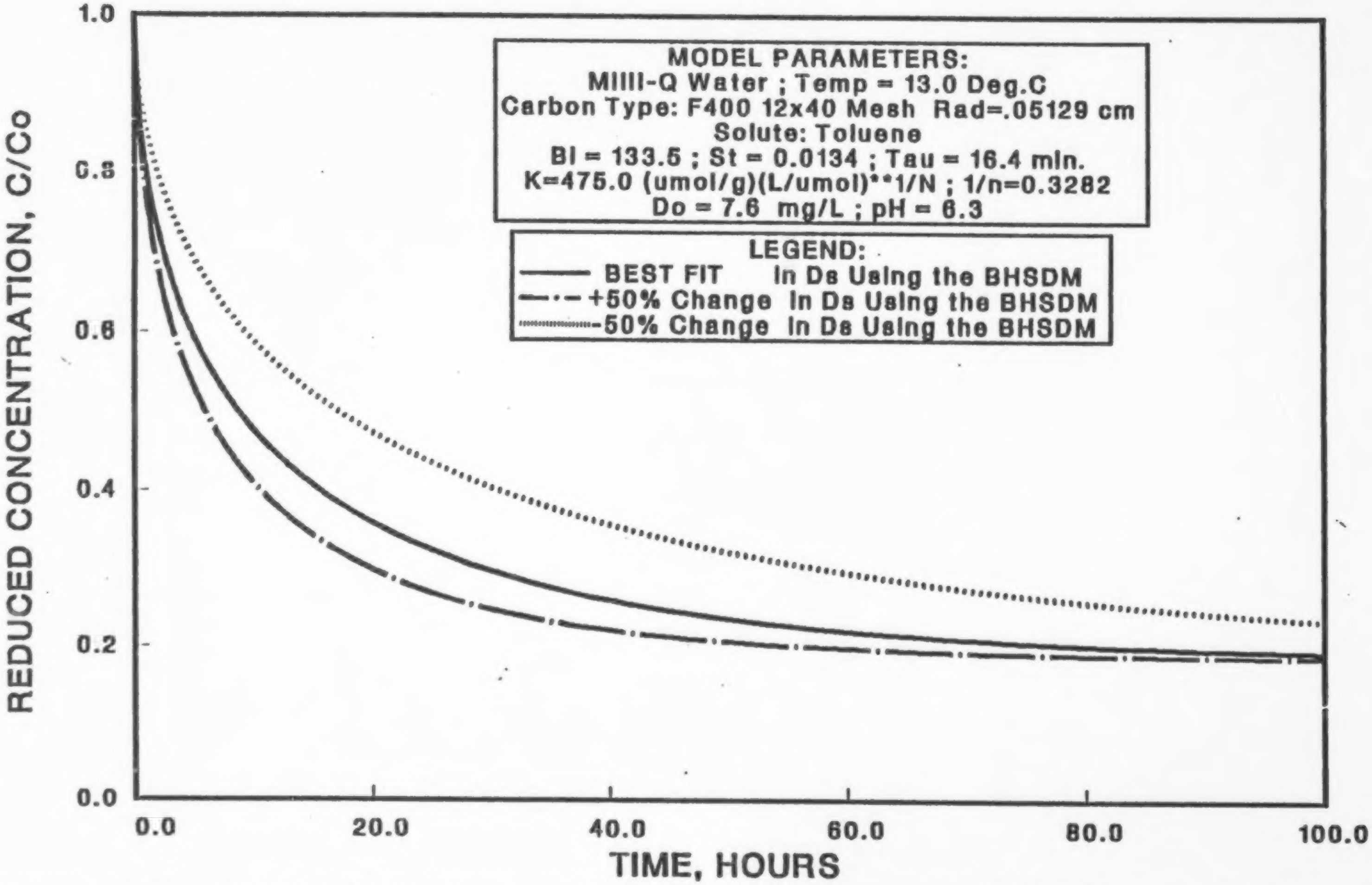

Figure VII-8. BHSDM Sensitivity Analysis of +/- 50% D_s for Toluene in Milli-Q Water and (12x40) F-400 Carbon (Bi = 133.5 ; C_o = 372.4 µg/L).

BHSDM calculations for various Biot numbers. At short times, film transfer limits the rate and the initial part of the curve is more impacted by film transfer, while the at longer times, surface diffusion limits the rate and the later part of the curve is impacted by surface diffusivity. Figures VII-1 through VII-4 display the sensitivity analysis for the film transfer coefficient, and Figures VII-5 through VII-8 display the sensitivity analysis for the surface diffusion coefficient. These figures demonstrated that for Biot numbers greater than about 30, film transfer had little impact on the BHSDM calculations. It is likely that these results are only valid for the particular Freundlich K's and 1/n's in this study.

B. Sensitivity Analysis of the Freundlich Isotherm Parameters K and 1/n in the Determination of the Surface Diffusion Rate

The Freundlich isotherm parameters K and 1/n must also be well defined to accurately estimate the surface diffusivity. Table VI-1 displays the upper and lower bounds of the 95% confidence limits. A sensitivity analysis of the Freundlich isotherm parameters, K and 1/n, was performed using the 95% confidence limits for trichloroethene, tetrachloroethene, and toluene, and are displayed in Figures VII-9 through VII-14, respectively. As shown in Figures VII-9, VII-10, and VII-11, calculations were sensitive to the 95% confidence limits in the Freundlich isotherm parameter K for trichloroethene, while the 95% confidence limits in the Freundlich isotherm constant K tetrachloroethene and toluene had less impact on BHSDM calculations. Although the 95% confidence limits for the Freundlich isotherm parameter K have a significant impact on the predictive profiles, the capacities observed in the DCBR studies agreed fairly well with isotherm capacities as shown in Table VI-3.

As shown in Figures VII-12, VII-13, and VII-14, the Freundlich isotherm parameter 1/n for trichloroethene, tetrachloroethene, and toluene had little impact on the BHSDM calculations.

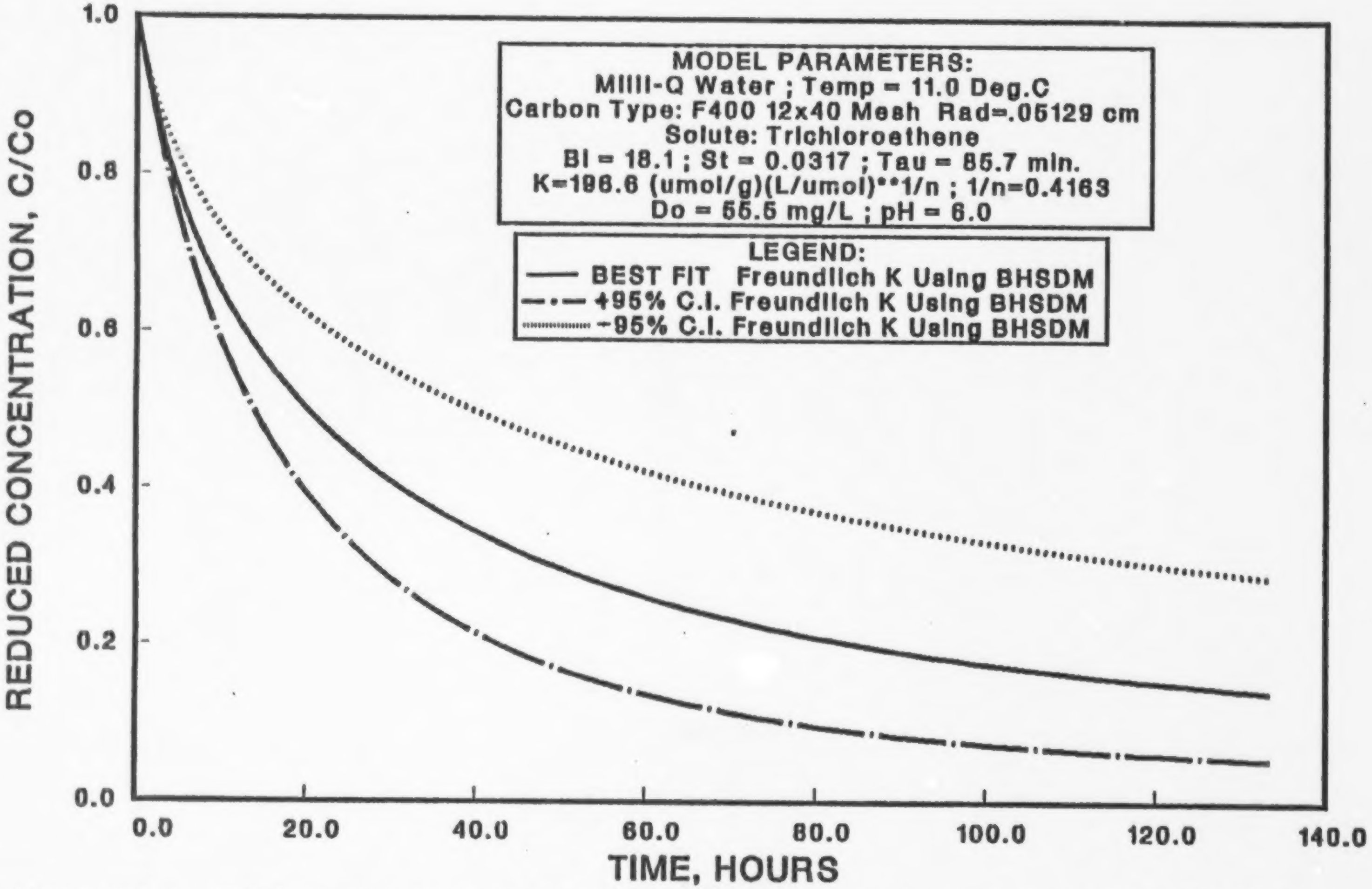

Figure VII-9. BHSDM Sensitivity Analysis of +/- 95% Confidence Interval for the Freundlich K for Trichloroethene in Milli-Q Water and (12x40) Carbon (Bi=18.1 ; C_0=1322.7 μg/L).

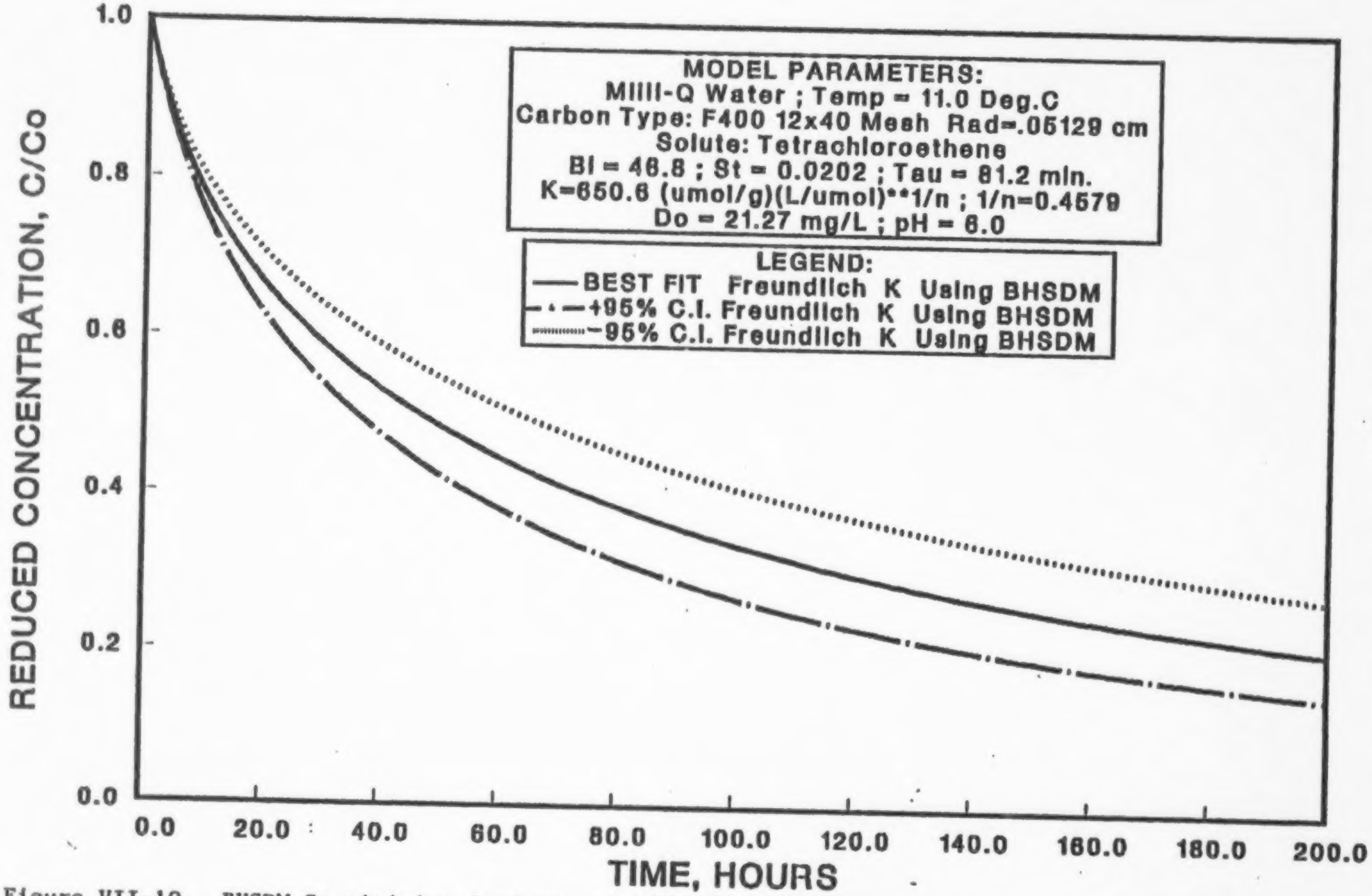

Figure VII-10. BHSDM Sensitivity Analysis of +/- 95% Confidence Interval for the Freundlich K for Tetrachloroethene in Milli-Q Water and (12x40) F-400 Carbon (Bi=46.8 ; C_o=1438.4 µg/L).

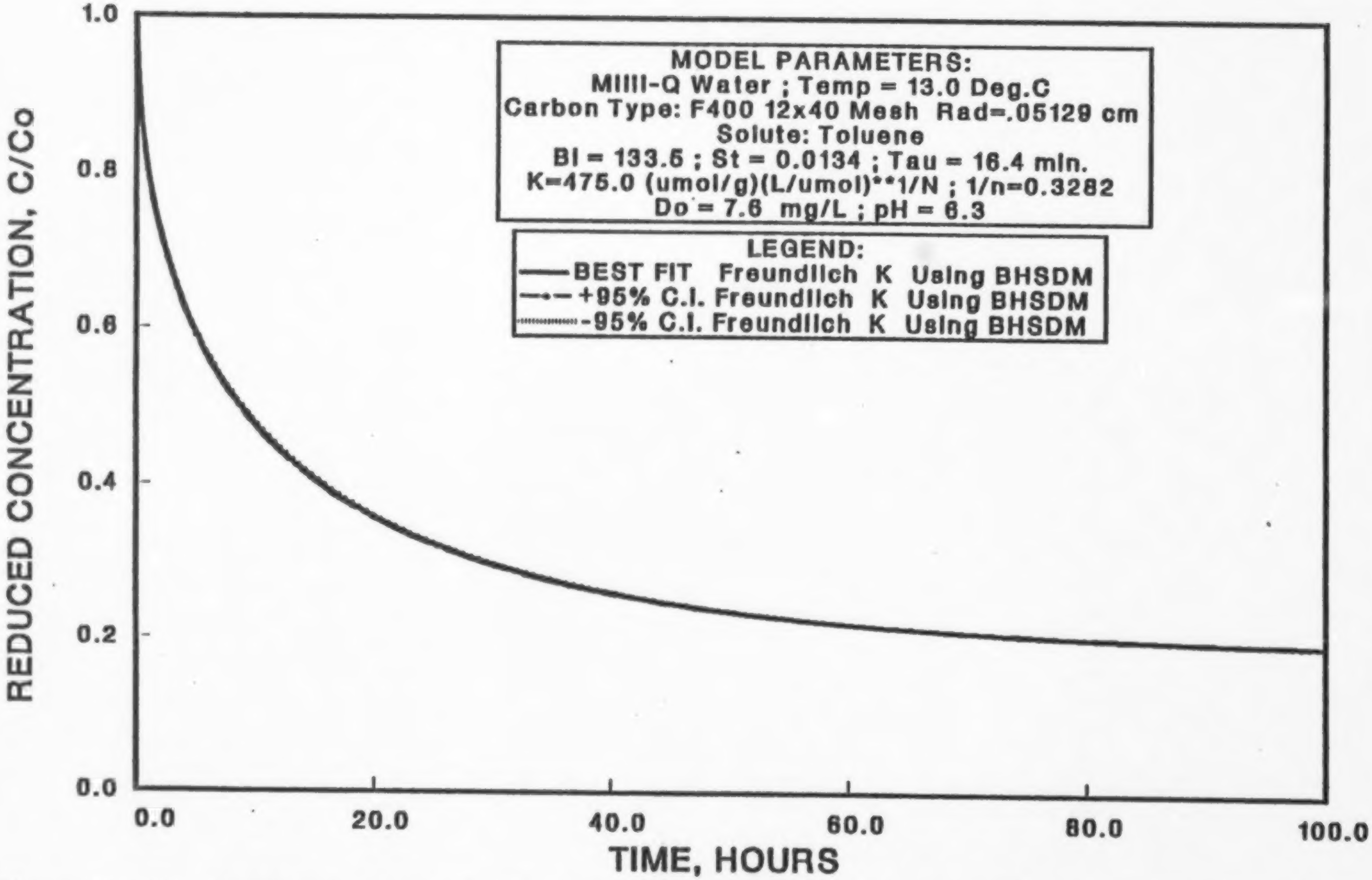

Figure VII-11. BHSDM Sensitivity Analysis of +/- 95% Confidence Interval for the Freundlich K for Toluene in Milli-Q Water and (12x40) F-400 Carbon (Bi=133.5 ; C_o= 372.4 µg/L).

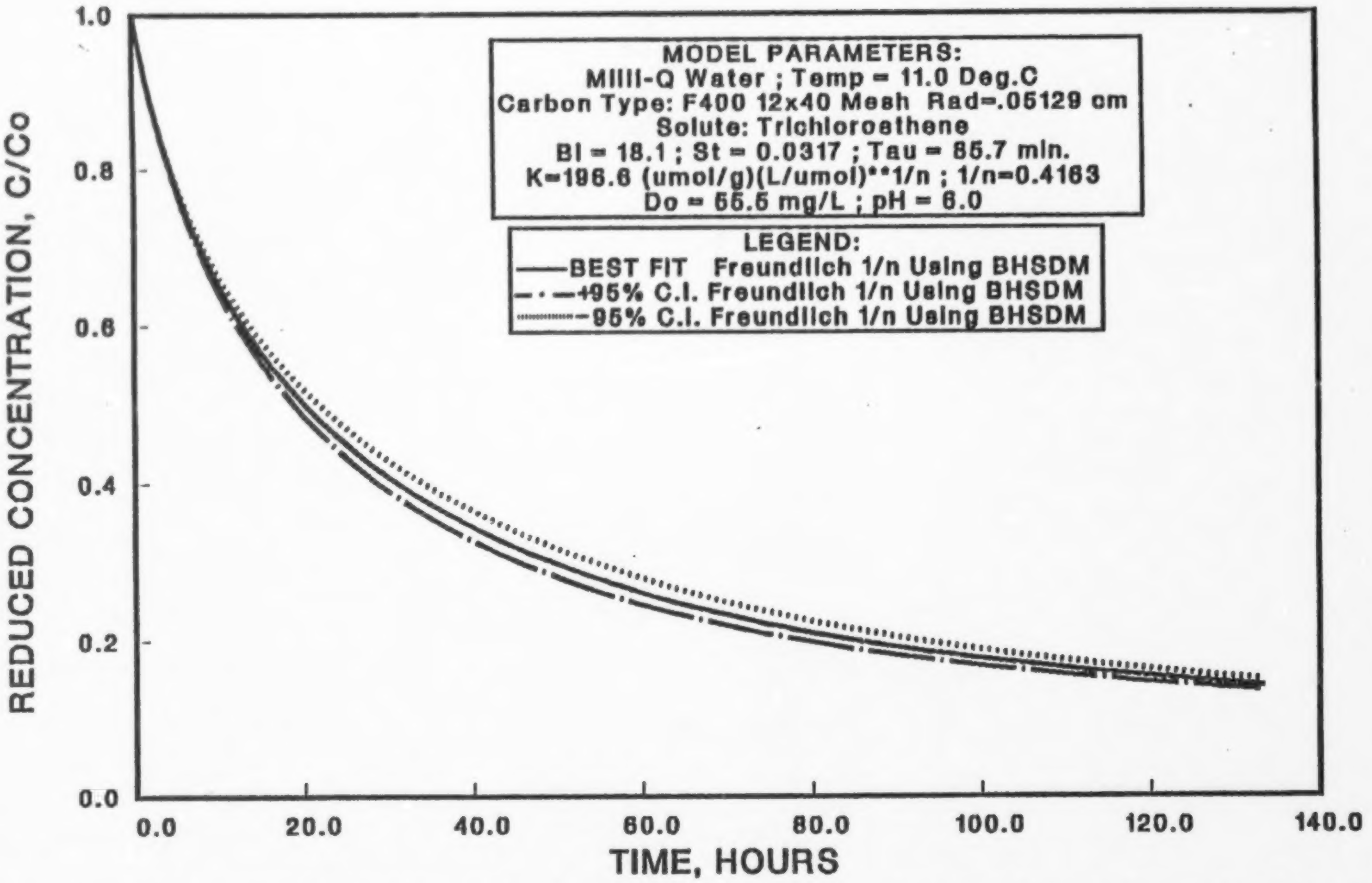

Figure VII-12. BHSDM Sensitivity Analysis of +/- 95% Confidence Interval for the Freundlich 1/n for Trichloroethene in Milli-Q Water and (12x40) F-400 Carbon (Bi=18.1 ; C_0=1322.7 µg/L).

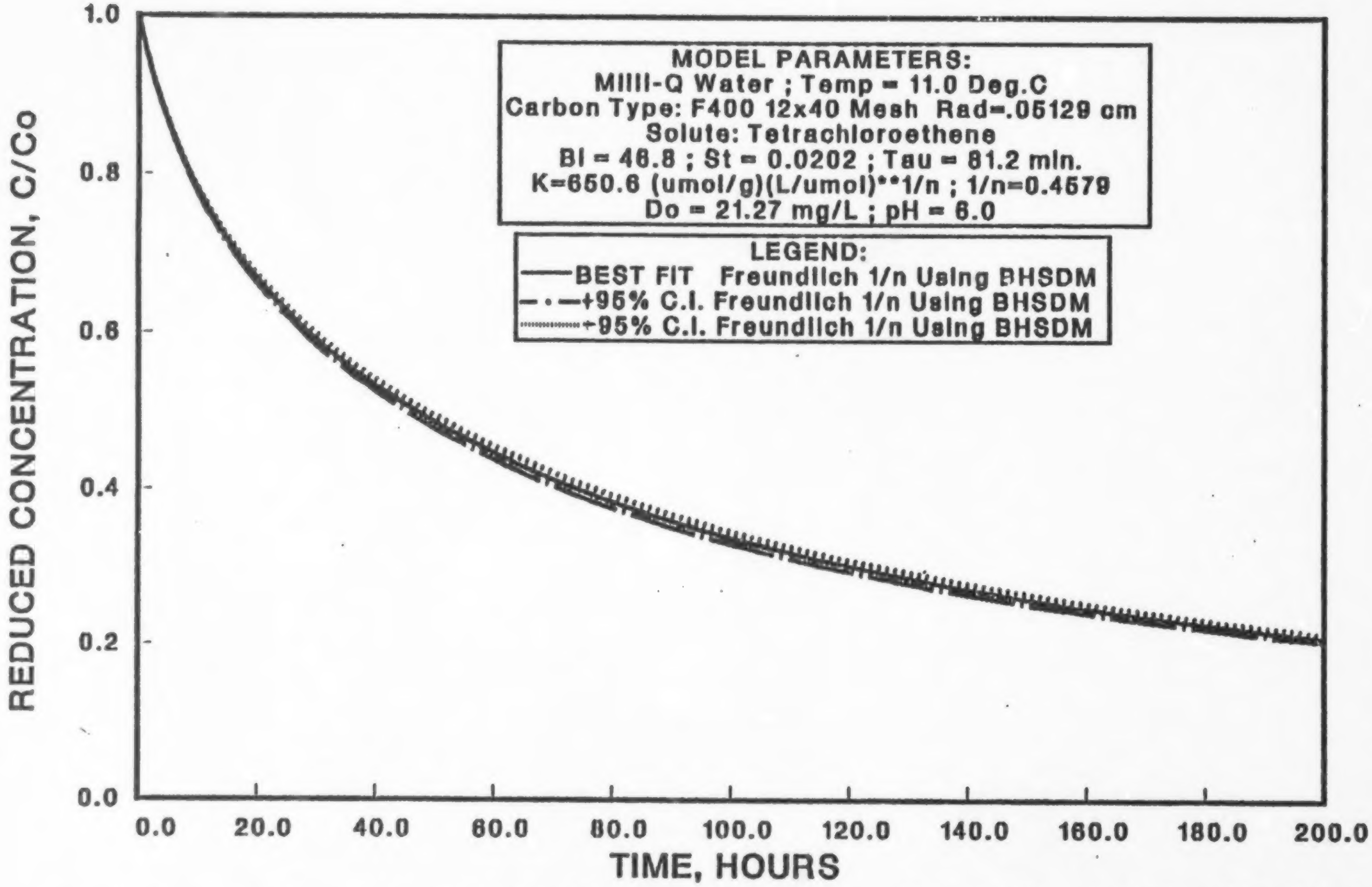

Figure VII-13. BHSDM Sensitivity Analysis of +/- 95% Confidence Interval for the Freundlich 1/n for Tetrachloroethene in Milli-Q Water and (12x40) F-400 Carbon (Bi=46.8 ; C_o=1438.4 µg/L).

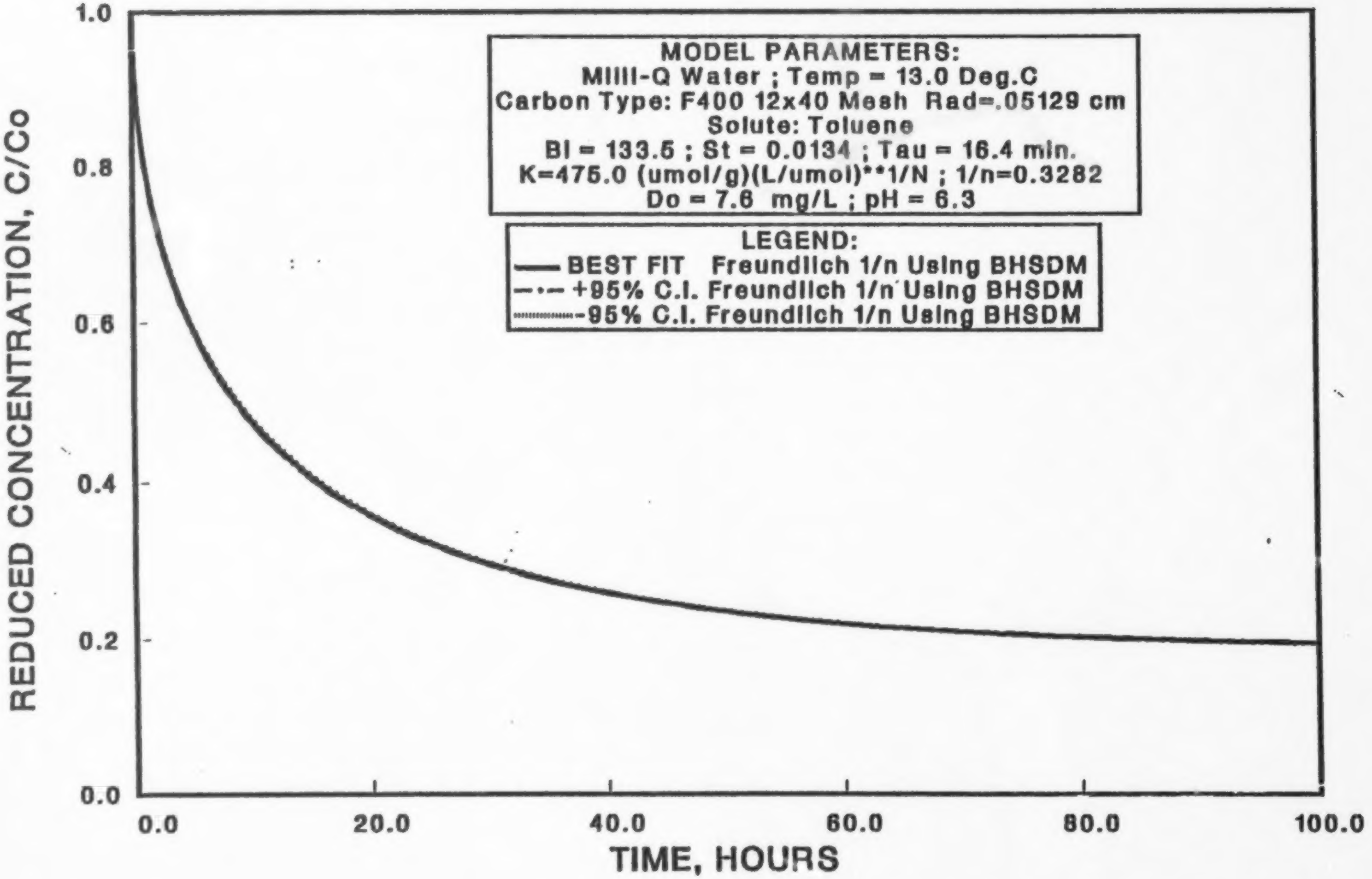

Figure VII-14. BHSDM Sensitivity Analysis of +/- 95% Confidence Interval for the Freundlich 1/n for Toluene in Milli-Q Water and (12x40) F-400 Carbon (Bi = 133.5 ; C_o = 372.4 μg/L).

VIII. CORRELATIONS FOR THE DETERMINATION OF SURFACE DIFFUSIVITIES

Correlations were developed to determine the surface diffusivities from the physical properties of the adsorbent and the known chemical properties of the adsorbates. The properties of adsorbates that where investigated for possible correlation were: 1) the boiling point of the adsorbates, 2) the liquid diffusivity of the adsorbates and the partitioning evaluated at the initial concentration of the adsorbates 3) the liquid diffusivity and the average driving force of the adsorbates and 4) the self-diffusivity and the partitioning evaluated at the initial concentration of the adsorbates.

A. Correlation Based on the Boiling Point of the Adsorbates

A method which was proposed by Suzuki et. al. (1975), is given in the following equation:

$$D_s = A \exp^{[-B\ (T_b/T)]} \qquad \text{(VIII-1)}$$

in which, T_b is the boiling point temperature of the adsorbate in °K and T is the temperature of the batch rate study in °K.

The basis for this equation is to relate the activation energy in the surface diffusion process to the heat of vaporization for a given solute.

B. Correlation Based on the Liquid Diffusivity and the Partitioning Evaluated at the Initial Concentration of the Adsorbates

The basis for this equation was to set the effective solid diffusion flux equal to a pore diffusion flux times a constant. This constant was defined as the pore to surface diffusion flux ratio (PSDFR). The following equation was developed from the total adsorbent phase mass flux, J_{tot}, given in Figure III-1:

$$J_{tot} = - D_s \frac{\partial q}{\partial r} - \frac{D_1 \varepsilon_p}{\tau_p} \frac{\partial C_p}{\partial r} \qquad \text{(VIII-2)}$$

The following equation is a simplification of Equation VIII-2 which represents the total flux as an effective solid diffusion flux:

$$J_{tot} = - D'_s \frac{\partial q}{\partial_r} \qquad \text{(VIII-3)}$$

where

$$\text{Surface Flux Contribution} = - D_s \frac{\partial q}{\partial r}$$

$$\text{Pore Flux Contribution} = - \frac{D_1 \varepsilon_p}{\tau_p} \frac{\partial C_p}{\partial r}$$

$$\text{Effective Solid Flux Contribution} = - D'_s \frac{\partial q}{\partial_r}$$

The pore diffusion coefficient was given as:

$$D_p = \frac{D_1}{\tau_p} \qquad \text{(VIII-4)}$$

Values for the tortuosity, τ_p, range between 2 and 6. A value of 1.0 was chosen for τ_p, because it would give the largest flux due to the contribution of pore diffusion. However, this was not important, because the effects of τ_p were taken into account in the pore to surface diffusion flux ratio, PSDFR. Setting the Equation VIII-2 equal to Equation VIII-3 yields the following equation:

$$-D'_s \frac{\partial q}{\partial r} = -\frac{D_1 \varepsilon_p}{\tau_p} \frac{\partial C_p}{\partial r} - D_s \frac{\partial q}{\partial r} \qquad \text{(VIII-5)}$$

Rearranging Equation VIII-5 and using the chain rule results in Equation VIII-6:

$$-D'_s \frac{\partial q}{\partial r} = -\left[\frac{D_1 \varepsilon_p}{\tau_p} \frac{\partial C_p}{\partial q} + D_s \right] \frac{\partial q}{\partial r} \qquad \text{(VIII-6)}$$

Setting the surface diffusion coefficient, D_s, equal to the pore diffusion flux times a constant (PSDFR − 1) yields:

$$D_s = \left[\frac{D_1 \varepsilon_p}{\tau_p} \frac{\partial C_p}{\partial q} (\text{PSDFR} - 1) \right] \qquad \text{(VIII-7)}$$

Substituting Equation VIII-7 into Equation VIII-6 and simplifying results in the following equation:

$$D'_s = \frac{\varepsilon_p D_1}{\tau_p \rho_a} \frac{\partial C_p}{\partial q} (\text{PSDFR}) \qquad \text{(VIII-8)}$$

Taking the partial derivative of the Freundlich isotherm equation with respect to the liquid-phase concentration, C_p results in this equation:

$$\frac{\partial q}{\partial C_p} = 1/n\ K\ C_p^{(1/n - 1)} \qquad \text{(VIII-9)}$$

The quantity, $\partial q/\partial C_p$, was determined from the Freundlich isotherm equation. Partitioning is defined as the ratio of the concentration in the adsorbent phase to the concentration in the fluid phase. The average partitioning was taken over the entire concentration range. The lower limit of the concentration was zero and the upper limit of the concentration was the initial concentration, C_o. The resulting equation is:

$$\overline{\frac{\partial q}{\partial C_p}} = \frac{\int (\partial q/\partial C_p)\ dC_p}{\int dC_p} \qquad \text{(VIII-10)}$$

Substituting the quantity, $\partial q/\partial C_p$, into Equation VIII-10 resulted in the following equation:

$$\overline{\frac{\partial q}{\partial C_p}} = \frac{\int (1/n\ K\ C_p^{(1/n\ -\ 1)}\ dC_p}{\int dC_p} \qquad \text{(VIII-11)}$$

Integrating and evaluating the equation at its limits yields:

$$\overline{\frac{\partial q}{\partial C_p}} = \frac{K\ C_o^{1/n}}{C_o} \qquad \text{(VIII-12)}$$

Substituting Equation VIII-12 into Equation VIII-8 results in the following equation:

$$D'_s = \frac{\varepsilon_p\ D_1\ C_o}{\tau_p\ \rho_a\ K\ C_o^{1/n}} \quad \text{(PSDFR)} \qquad \text{(VIII-13)}$$

C. Correlation Based on the Liquid Diffusivity and the Average Driving Force of the Adsorbates

The correlation which was based on the liquid diffusivity and the average driving force of the adsorbates was used to take the average of that which appears in Equation VIII-8. The lower limit of the concentration was zero and the upper limit of the concentration was the initial concentration. The result was:

$$\overline{\frac{\partial C_p}{\partial q}} = \frac{\int 1/(\partial q/\partial C_p)\, dC_p}{\int dC_p} \qquad \text{(VIII-14)}$$

Substituting the quantity, $\partial q/\partial C_p$, into Equation VIII-14 results in the following equation:

$$\overline{\frac{\partial C_p}{\partial q}} = \frac{\int 1[(1/n\ K\ C_p^{(1/n - 1)}}{\int dC_p}\, dC_p \qquad \text{(VIII-15)}$$

Integrating and evaluating the equation at its limits yields the following equation:

$$\overline{\frac{\partial C_p}{\partial q}} = \frac{C_o^{(1 - 1/n)}}{(1/n)\ K\ (2 - 1/n)} \qquad \text{(VIII-16)}$$

Substituting Equation VIII-16 into Equation VIII-8 resulted in the following equation:

$$D'_s = \frac{\varepsilon_p\ D_l\ C_o^{(1 - 1/n)}}{\tau_p\ \rho_a\ (1/n)\ K\ (2 - 1/n)} \quad \text{(PSDFR)} \qquad \text{(VIII-17)}$$

D. Correlation Based on the Self-Diffusivity and the Partitioning Evaluated at the Initial Concentration of the Adsorbates

A correlation was developed to relate the surface diffusivity to the self-diffusivity of the adsorbates. Due to adsorption, a condensed state of the solute can exist. This condensed solute may diffuse at a rate which is more like the self-diffusivity of the molecule as opposed to the liquid diffusivity of the molecule. To express this, the self-diffusivity was determined from a correlation given by Bird, Stewart, and Lightfoot (1960):

$$D_{AA} = \frac{k\ T}{2\pi\ \mu_A} \left[\frac{N_o}{V_b} \right]^{1/3} \qquad \text{(VIII-18)}$$

Equation VIII-18 was based on hydrodynamical theory. It takes as its starting point the Stokes-Einstein equation. The assumptions of this equation are: 1) there is no tendency for the fluid to stick at the surface of the diffusing particle, and 2) the molecules are all alike and can be arranged in a cubic lattice with all molecules touching.

Equation VIII-18 was substituted into Equation VIII-13 in place of D_1 to yield the final equation based on self-diffusion:

$$D'_s = \frac{\varepsilon_p\ D_{AA}\ C_o}{\tau_p\ \rho_a\ K\ C_o^{1/n}} \quad \text{(PSDFR)} \qquad \text{(VIII-19)}$$

E. Results and Discussion

The experimentally measured surface diffusivities of various synthetic organic compounds were obtained from the literature (Crittenden, 1978; Pirbazari, 1981; Thacker, 1983; van Vliet et. al., 1981; Liu et. al., 1981; and Sabin, 1981). The important parameters, along with the calculated contribution of the diffusion flux are presented in Tables VIII-2 through VIII-4.

For the Suzuki method, measured surface diffusivities of aliphatic, halogenated hydrocarbons were plotted versus the ratio of the boiling point of the adsorbate to the temperature of the experiment. The experimental surface diffusivities, along with the boiling points of the adsorbates are displayed in Table VIII-1. The data were fit using the International Mathematical and Statistical Libraries (IMSL) nonlinear least squares method and was determined by minimizing the sum of the differences between the experimental surface diffusivities and the ratio of the boiling point of the adsorbate to the

Table VIII-1. Data for the Correlation Based on the Boiling Points of the Adsorbates

Compound	Initial Concentration 10^6 x Molar	Water Matrix Carbon Type	Temperature of Experiment (°K)	Boiling Point of Adsorbate (°K)	Experimental Surface Diffusivity $D_s \times 10^{10}$ (cm^2/s)	References
Benzene	5.76	Milli-Q F-400 (16x20)	295.15	353.15	13.0	Pirbazari * (1981)
Bromodichloromethane	0.76	Milli-Q F-400 (16x20)	295.15	360.15	3.3	Thacker (1981)
p-bromophenol	480.0	Milli-Q F-400 (12x40)	295.15	509.15	856.0	Crittenden * (1978)
Carbon tetrachloride	1.21	Milli-Q F-400 (16x20)	295.15	350.15	3.2	Pirbazari (1981)
Chloroform	1.67	Milli-Q F-400 (16x20)	295.15	334.15	32.0	Thacker (1981)
Chloroform	3.10	Milli-Q HD-3000 (12x40)	293.15	334.15	2.9	Sabin * (1981)
Chloroform	3.74	Milli-Q HD-4000 (50x100)	297.15	334.15	2.2	Sabin * (1981)
cis-1.2 dichloroethene	5.23	Milli-Q F-400 (12x40)	286.15	333.15	27.0	This Study
p-Dichlorobenzene	1.07	Milli-Q F-400 (50x60)	295.15	445.15	800.0	Pirbazari * (1981)
1.2 Dichloroethane	1.25	Milli-Q F-400 (12x40)	295.15	356.15	17.7	Weber et. al. (1982)
Phenol	4600.0	Milli-Q F-400 (16x20)	295.15	455.15	353.0	Crittenden * (1978)
Tetrachloroethene	9.07	Milli-Q F-400 (60x80)	284.15	394.15	1.5	This Study
Tetrachloroethene	8.67	Milli-Q F-400 (12x40)	284.15	394.15	0.5	This Study
Toluene	4.04	Milli-Q F-400 (12x40)	286.15	383.15	18.0	This Study *
Trichloroethene	10.1	Milli-Q F-400 (60x80)	284.15	360.15	4.3	This Study
Trichloroethene	10.0	Milli-Q F-400 (12x40)	284.15	360.15	3.1	This Study
Trichloroethene	10.9	Thawed Water F-400 (12x40)	284.15	360.15	2.6	This Study
Trichloroethene	9.46	Thawed Water WV-G (12x40)	284.15	360.15	2.8	This Study
Trichloroethene	10.0	Milli-Q WV-G (12x40)	284.15	360.15	3.3	This Study

* Indicates the data were not used in determining the correlation

temperature of the batch rate study. The final form for the Suzuki equation is:

$$D_s = 4.73 \times 10^{-9} \exp^{[-11.665\ (T_b/T)]} \qquad \text{(VIII-20)}$$

The correlation coefficient for the Suzuki method was 0.7016.

The correlation which was based on the liquid diffusivity and the partitioning evaluated at the initial concentration of the adsorbates was determined by plotting experimental surface diffusivities versus the pore diffusion flux contribution (PDFC) as shown in the following equation:

$$\text{PDFC} = \frac{\varepsilon_p D_l C_o}{\tau_p \rho_a K C_o^{1/n}} \qquad \text{(VIII-21)}$$

The experimental surface diffusivities and the PDFC from Table VIII-2 were fit using the International Mathematical and Statistical Libraries (IMSL) linear least squares method and was determined by minimizing the sum of the differences between the experimental surface diffusivities and the those calculated by equation VIII-21. The equation was of the form Y = A * X. The slope, A, corresponds to the pore to surface diffusion flux ratio, PSDFR. Figure VIII-1 displays the data along with the best linear fit and the 95% confidence bands on a log-log plot. The best fit slope of the line was 6.5814 with 95% confidence limits of 4.603 to 8.560. The correlation coefficient for this method was 0.8987. This correlation included data of halogenated, one and two carbon molecules, and some substituted, aromatic compounds for two types of carbons. Some solutes, however, were not included in the correlation. Two of the solutes were run on a different type of carbon. The HD-3000 and HD-4000 carbons have a large volume of macropores, while the WV-G and the F-400 carbons have a large volume of micropores. Also p-toluene sulfonate and phenol, which were conducted by van Vliet et. al., were excluded, since the

Table VIII-2. Comparison of the Calculated and Observed Surface Diffusivities Based on the Liquid Diffusivity and the Partitioning Evaluated at the Initial Concentration of the Adsorbates

Compound	Initial Concentration 10^6 x Molar	Water Matrix Carbon Type	Freundlich Isotherm Parameters K $(\mu g/g)(L/\mu g)^{1/n}$ or ^a^Solute Distribution Parameter for a Fixed-Bed	1/n (Dimensionless) (Dimensionless)	Temperature (°C)	Calculated PSDC Using Equation VIII-21 $D_s x 10^{10}$ (cm^2/s)	Experimental Surface Diffusivity $D_s x 10^{10}$ (cm^2/s)	Individual Pore to Surface Diffusion Flux Ratio (PSDFR)	References
Benzene	5.76	Milli-Q F-400 (16x20)	1140.0	0.3980	22.0	2.63	13.0	4.91	Pirbazari (1981)
p-bromophenol	5000.0	Milli-Q F-400 (12x40)	^a^4100		22.0	17.40	856.0	49.21	Crittenden * (1978)
p-bromophenol	480.0	Milli-Q F-400 (16x20)	^a^4300		22.0	3.74	200.0	58.42	Lin et. al. * (1981)
Bromodichloromethane	0.76	Milli-Q F-400 (16x20)	142.98	0.7450	22.0	1.83	3.3	1.80	Thacker (1982)
Carbon tetrachloride	1.21	Milli-Q F-400 (16x20)	224.0	0.6300	22.0	2.12	3.2	1.51	Pirbazari (1981)
Chloroform	1.67	Milli-Q F-400 (16x20)	42.2	0.7520	22.0	7.89	32.0	4.16	Thacker (1981)
Chloroform	3.10	Milli-Q HD-3000 (12x40)	106.0	0.6470	20.0	6.83	2.9	.42	Sabin * (1981)
Chloroform	3.74	Milli-Q HD-4000 (50x100)	159.0	0.6250	24.0	6.22	2.2	.35	Sabin * (1981)
cis-1,2 dichloroethene	5.23	Milli-Q F-400 (12x40)	357.0	0.5618	12.0	2.44	27.0	11.10	This Study
1,2 Dichloroethane	1.25	Milli-Q F-400 (12x40)	37.9	0.8316	22.0	4.57	17.7	3.87	Weber et. al.* (1982)
3,5 dichlorophenol	1000.0	Milli-Q F-400 (16x20)	^a^2600		22.0	25.30	155.0	6.12	Thacker (1981)
3,5 dimethylphenol	1000.0	Milli-Q F-400 (16x20)	^a^2500		22.0	26.10	94.8	3.63	Thacker (1981)
Dodecyl Benzene Sulfonate	2900.0	Milli-Q F-400 (16x20)	^a^3900		22.0	9.21	46.9	5.09	Crittenden (1978)

* Indicates the data were not used in the determining the correlation (Continued)

Table VIII-2 (Continued). Comparison of the Calculated and Observed Surface Diffusivities Based on the Liquid Diffusivity and the Partitioning Evaluated at the Initial Concentration of the Adsorbates

Compound	Initial Concentration 10^6 x Molar	Water Matrix Carbon Type	Freundlich Isotherm Parameters K $(\mu g/g)(L/\mu g)^{1/n}$ or ^{a}Solute Distribution Parameter for a Fixed-Bed	1/n (Dimensionless) (Dimensionless)	Temperature (°C)	Calculated PDFC Using Equation VIII-22 $D_s x10^{10}$ (cm^2/s)	Experimental Surface Diffusivity $D_s x10^{10}$ (cm^2/s)	Individual Pore to Surface Diffusion Flux Ratio (PSDFR)	References
Phenol	530.0	Milli-Q F-400 (40x50)	^{a}2240		22 .0	35.90	12.4	0.34	van Vliet *et. al.* (1981) *
Phenol	4600.0	Milli-Q F-400 (16x20)	^{a}2600		22.0	31.00	353.0	11.4	Crittenden (1976)
Tetrachloro-ethene	9.07	Milli-Q F-400 (60x80)	10388.8	0.4579	11.0	0.26	1.5	5.77	This Study
Tetrachloro-ethene	8.67	Milli-Q F-400 (12x40)	10388.8	0.4579	11.0	0.18	0.5	2.78	This Study
Toluene	4.04	Milli-Q F-400 (12x40)	991.7	0.3282	13.0	0.28	18.0	64.3	This Study *
p-Toluene Sulfonate	100.0	Milli-Q F-400 (16x20)	^{a}3100		22.0	20.00	191.0	9.55	Crittenden (1976)
p-Toluene Sulfonate	77.0	Milli-Q F-400 (40x50)	^{a}2090		22.0	29.50	23.3	0.79	van Vliet *et. al.* (1981) *
Trichloro-ethene	10.1	Milli-Q F-400 (60x80)	3389.7	0.4163	11.0	1.00	4.3	4.30	This Study
Trichloro-ethene	10.0	Milli-Q F-400 (12x40)	3389.7	0.4163	11.0	1.00	3.1	3.10	This Study
Trichloro-ethene	10.9	Thawed Wenonah F-400 (12x40)	3389.7	0.4163	11.0	1.06	2.6	2.40	This Study
Trichloro-ethene	9.46	Thawed Wenonah WV-G (12x40)	3261.9	0.4073	11.0	1.17	2.8	2.40	This Study
Trichloro-ethene	10.0	Milli-Q WV-G (12x40)	3261.9	0.4073	11.0	1.22	3.3	2.70	This Study

* Indicates the data were not used in the determining the correlation

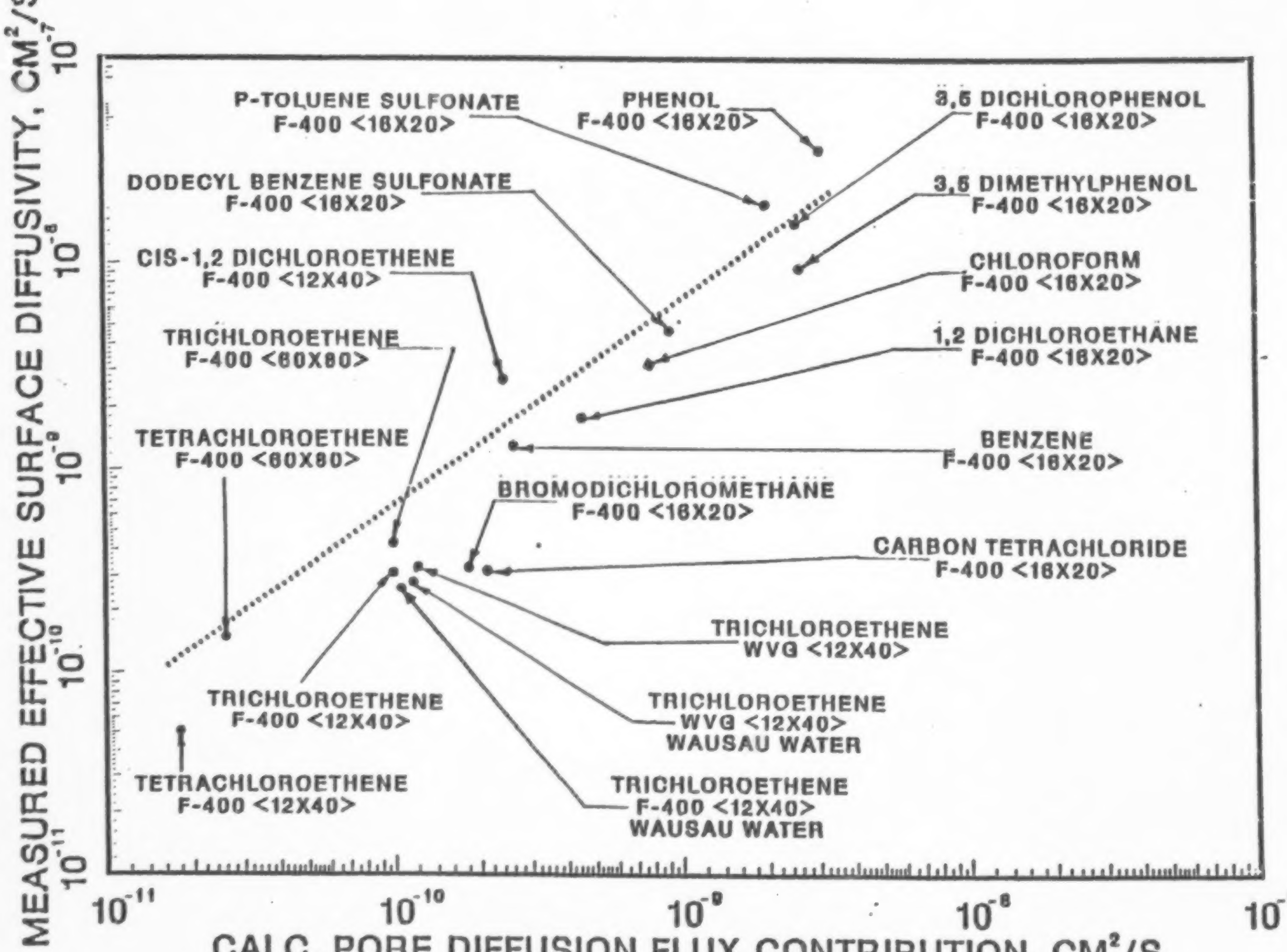

Figure VIII-1. Comparison Between the Measured Surface Diffusivities and the Pore Diffusion Flux Contribution Using the Liquid Diffusivity Correlation. Carbon Type and Mesh Size is Indicated.

pore flux rate was greater. This was the only occurrence of the pore flux rate being greater in the literature. Consequently, it was not used, because it would affect the PSDFR determination. The p-bromophenol and toluene surface diffusivities were excluded, since these compounds gave a pore to surface diffusion flux ratio that was much greater than the average pore to surface diffusion flux ratio. The exclusion of these data allow the correlation to underestimate the surface diffusivities of some solutes.

The correlation which was based on the liquid diffusivity and on the average driving force of the adsorbates was determined by plotting experimental surface diffusivities versus the pore diffusion flux contribution (PDFC) from the following equation:

$$\mathrm{PDFC} = \frac{\varepsilon_p D_l C_o^{(1 - 1/n)}}{\tau_p \rho_a (1/n) K (2 - 1/n)} \qquad \text{(VIII-22)}$$

The experimental surface diffusivities and the PDFC from Table VIII-3 were fit using the IMSL linear least squares. The best fit slope of the line was 4.372 with 95% confidence limits of 2.337 to 6.367. The correlation coefficient for this method was 0.8849. As shown in Table VIII-3, only the data for the aliphatic, halogenated, volatile organic compounds and the two carbons of interest were used to determine the PSDFR.

The correlation which was based on the self-diffusivity and the partitioning evaluated at the initial concentration of the adsorbates was determined by plotting experimental surface diffusivities versus the pore diffusion flux contribution (PDFC) as shown in the following equation:

$$\mathrm{PDFC} = \frac{\varepsilon_p D_{AA} C_o}{\tau_p \rho_a K C_o^{1/n}} \qquad \text{(VIII-23)}$$

The experimental surface diffusivities from Table VIII-4 and the PDFC

Table VIII-8. Comparison of the Calculated and Observed Surface Diffusivities Based on the Liquid Diffusivity and on the Average Driving Force of the Adsorbates

Compound	Initial Concentration 10^6 x Molar	Water Matrix Carbon Type	Freundlich Isotherm Parameters K (μg/g)(L/μg)$^{1/n}$	 1/n (Dimensionless)	Temperature (°C)	Calculated ADFC Using Equation VIII-22 $D_s x10^{10}$ (cm^2/s)	Experimental Surface Diffusivity $D_s x10^{10}$ (cm^2/s)	References
Benzene	5.76	Milli-Q F-400 (16x20)	1140.0	0.3980	22.0	4.12	13.0	Pirbazari * (1981)
Bromodichloro-methane	0.76	Milli-Q F-400 (16x20)	143.0	0.7450	22.0	1.94	3.3	Thacker (1981)
Carbon tetrachloride	1.21	Milli-Q F-400 (16x20)	224.0	0.6300	22.0	2.46	3.2	Pirbazari (1981)
Chloroform	1.67	Milli-Q F-400 (16x20)	42.2	0.7520	22.0	8.56	32.0	Thacker (1981)
Chloroform	3.10	Milli-Q HD-3000 (12x40)	106.0	0.6470	22.0	2.91	2.9	Sabin * (1981)
Chloroform	3.74	Milli-Q HD-4000 (50x100)	159.0	0.6250	22.0	7.24	2.2	Sabin * (1981)
cis-1,2 dichloro-ethene	5.23	Milli-Q F-400 (12x40)	357.0	0.5618	12.0	3.02	27.0	This Study
1,2 Dichloro-ethane	1.25	Milli-Q F-400 (12x40)	37.9	0.8316	22.0	4.71	17.7	Weber et. al. (1982)
Tetrachlor-ethene	9.07	Milli-Q F-400 (60x80)	10888.8	0.4579	11.0	0.35	1.5	This Study
Tetrachloro-ethene	8.67	Milli-Q F-400 (12x40)	10888.8	0.4579	11.0	0.32	0.48	This Study
Toluene	4.04	Milli-Q F-400 (12x40)	991.7	0.3282	13.0	5.06	18.00	This Study *
Trichloroethene	10.1	Milli-Q F-400 (60x80)	3389.7	0.4163	11.0	1.71	4.30	This Study
Trichloroethene	10.0	Milli-Q F-400 (12x40)	3389.7	0.4163	11.0	1.52	3.10	This Study
Trichloroethene	10.9	Thawed Wausau F-400 (12x40)	3389.7	0.4163	11.0	1.79	2.6	This Study
Trichloroethene	9.46	Thawed Wausau WV-G (12x40)	3261.9	0.4073	11.0	1.80	2.8	This Study
Trichloroethene	10.0	Milli-Q WV-G (12x40)	3261.9	0.4073	11.0	1.87	3.3	This Study

* Indicates the data were not used in the determining the correlation

from Equation VIII-23 were again fit using the IMSL linear least squares. The best fit slope of the line was 4.549 with 95% confidence limits of 1.451 to 7.646. The correlation coefficient for this method was 0.7956. As shown in Table VIII-4, only the data for the aliphatic, halogenated, volatile organic compounds and the two carbons of interest were used.

The best correlation as determined from the correlation coefficient was based on the liquid diffusivity and the partitioning evaluated at the initial concentration of the adsorbates, Equation VIII-13. This equation is valid for halogenated, one and two carbon molecules, and some aromatic substituted organic compounds on F-400 and WV-G carbons. To make conservative estimates for fixed-bed design, Equation VIII-13 may be used to estimate the surface diffusivity of a variety of adsorbates. With the exception of data from van Vliet et. al., Equation VIII-13 either predicts the surface diffusivity with reasonable precision or a lower surface diffusivity for some compounds. See Table VIII-2 for a comparison between the measured and calculated surface diffusivity. Consequently, the calculated surface diffusivity can be used to make a conservative estimate of the mass transfer zone lengths in a fixed-bed (Hand et. al., 1984). This estimate would be conservative because, the surface diffusivity would either be correct or underestimated such that there would not be premature breakthrough of the solute in the fixed-bed.

Table VIII-4. Comparison of the Calculated and Observed Surface Diffusivities Based on the Self-Diffusivity and the Partitioning Evaluated at the Initial Concentration of the Adsorbates

Compound	Initial Concentration 10^6 x Molar	Water Matrix Carbon Type	Freundlich Isotherm Parameters K $(\mu g/g)(L/\mu g)^{1/n}$	 1/n (Dimensionless)	Temperature (°C)	Calculated MFPC Using Equation VIII-23 $D_s x 10^{10}$ (cm^2/s)	Experimental Surface Diffusivity $D_s x 10^{10}$ (cm^2/s)	References
Benzene	5.76	Milli-Q F-400 (16x20)	1140.0	0.3980	22.0	1.72	13.0	Pirbazari * (1981)
Bromodichloromethane	0.76	Milli-Q F-400 (16x20)	143.0	0.7450	22.0	6.71	3.3	Thacker (1981)
Carbon tetrachloride	1.21	Milli-Q F-400 (16x20)	224.0	0.6300	22.0	2.76	3.2	Pirbazari (1981)
Chloroform	1.67	Milli-Q F-400 (16x20)	42.2	0.7520	22.0	14.35	32.0	Thacker (1981)
Chloroform	3.10	Milli-Q HD-3000 (12x40)	106.0	0.6470	22.0	13.90	2.9	Sabin * (1981)
Chloroform	3.74	Milli-Q HD-4000 (50x100)	159.0	0.6250	22.0	11.60	2.2	Sabin * (1981)
cis-1,2 dichloroethene	5.23	Milli-Q F-400 (12x40)	357.0	0.5618	12.0	3.08	27.0	This Study
Tetrachloroethene	9.07	Milli-Q F-400 (60x80)	10388.8	0.4579	11.0	0.40	1.5	This Study
Tetrachloro-	8.67	Milli-Q F-400 (12x40)	10388.8	0.4579	11.0	0.39	0.48	This Study
Toluene	4.04	Milli-Q F-400 (12x40)	991.7	0.3282	13.0	6.47	18.00	This Study *
Trichloroethene	10.1	Milli-Q F-400 (60x80)	3389.7	0.4163	11.0	2.32	4.30	This Study
Trichloroethene	10.0	Milli-Q F-400 (12x40)	3389.7	0.4163	11.0	2.31	3.10	This Study
Trichloroethene	10.9	Thawed Wausau F-400 (12x40)	3389.7	0.4163	11.0	2.43	2.6	This Study
Trichloroethene	9.46	Thawed Wausau WV-G (12x40)	3261.9	0.4073	11.0	2.69	2.8	This Study
Trichloroethene	10.0	Milli-Q WV-G (12x40)	3261.9	0.4073	11.0	2.80	3.3	This Study

* indicates the data were not used in the determining the correlation

IX. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1.) For single-solute differential column batch reactor studies on both the 12x40 and 60x80 mesh carbons, the batch homogeneous surface diffusion model and the batch pore and surface diffusion model were able to simulate the concentration history profiles for the following volatile organic compounds: cis-1,2 dichloroethene, tetrachloroethene, toluene, and trichloroethene.

2.) The batch pore diffusion model was not able to predict the differential column batch reactor experimental data for single-solutes on the 12x40 and 60x80 mesh carbons. Therefore, surface diffusion was the controlling mechanism, because the pore diffusion mechanism alone did not predict the data. In addition, the batch pore and surface diffusion model, BPSDM, and the batch homogeneous surface diffusion model, BHSDM, were compared and it was found that the surface diffusivity did not change significantly from the BPSDM to the BHSDM. Therefore, the contribution to the total intraparticle flux from pore diffusion was negligible.

3.) The rates of uptake for trichloroethene in organic-free water and trichloroethene in thawed Wausau water matrix were almost identical. Since most of the VOCS were lost when the Wausau water was frozen, the background total organic carbon present had no effect on the adsorption rate or capacity of the carbon for the solute trichloroethene.

4.) It was not possible to conduct a multicomponent rate study on the raw Wausau water matrix, since degradation and proper selection of the carbon dosage were a problem. It was demonstrated that toluene degraded over a period of eight days to 30% of it original concentration, while the aliphatic halogenated hydrocarbons (cis-1,2 dichloroethene, trichloroethene, and tetrachloroethene), showed little degradation. Therefore, both degradation and adsorption were occurring in the multicomponent rate study. It was not possible to select an appropiate carbon dosage for a multicomponent rate study. If a high carbon dosage was chosen to observe the concentration history profile of the weakly adsorbing solute, it would result in a film transfer limited case for the strongly adsorbing solute. If a low carbon dosage was chosen to observe the concentration history profile of the strongly adsorbing solute, the concentration history for the weakly adsorbing solute would not be significantly depressed enough to see a profile and measurement of the intraparticle surface diffusion coefficient for the weakly adsorbing solute would not be possible.

5.) To properly design and evaluate DCBR data for the determination of the surface diffusivity, the following three requirements, which are based on the sensitivity analysis and other calculations, must be met: (a) the Biot numbers should be greater than 30, such that the surface diffusion is the rate-limiting mechanism, (b) the Stanton numbers should be less than or equal to 0.017, such that the concentration across the differential column is the same as the concentration in the DCBR reservoir, (c) the Freundlich isotherm constants, K and 1/n, are know to a high degree of accuracy.

6.) Four correlations were developed to determine the surface diffusivities of aliphatic, halogenated volatile organic compounds from the physical properties of the adsorbent and the chemical properties of the adsorbates. The properties of the adsorbates that were investigated for correlation were: (a) the boiling point of the adsorbates, (b) the liquid diffusivity of the adsorbates and the average driving force of the adsorbates, (c) the self diffusivity of the adsorbates and the partitioning evaluated at the initial concentration of the adsorbates, and (d) the liquid diffusivity of the adsorbates and the partitioning of the adsorbate between the bulk fluid and the adsorbent evaluated at the initial concentration of the adsorbates. The correlation coefficients for each of the above methods were 0.7016, 0.8849, 7699, and 0.9450, respectively. Since the correlation which was based on the liquid diffusivity and the partitioning of the adsorbate between the bulk fluid and the adsorbent evaluated at the initial concentration of the adsorbates was the best fit, other compounds from the literature were included in the correlation. The correlation is now applicable to halogenated, one and two carbon molecules, and some aromatic substituted organic compounds for the WV-G and F-400 carbons. The correlation coefficient for this method was 0.8987.

7.) This correlation is useful to make conservative estimates for fixed-bed design, because the correlation may be combined with the method developed by Hand et. al.; 1984, to calculate the mass transfer zone length in a fixed-bed.

Recommendations for Future Work

Based on the results of this work, the following areas are recommended for further study:

1.) More adsorbate-adsorbent systems need to be examined for the correlation which is based on the liquid diffusivity and the partitioning of the initial concentration of the adsorbates. Also the effect of particle size of the adsorbent and the initial concentration of the adsorbates should be examined to determine if a more general correlation for the surface diffusivities can be developed.

2.) Finally, the correlation which was based on the liquid diffusivity and the partitioning of the initial concentration, should be used to calculate the surface diffusivities of the compounds of interest in the Wausau water matrix. These surface diffusivities should be used in a column pore and surface diffusion model to see if the breakthrough profiles from a pilot column of the major components found in the Wausau water matrix can be predicted.

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APPENDIX 2. NOMENCLATURE

$Bi_{c,i}$	Biot number based on surface and pore diffusivity (dimensionless): $R\ k_{f,i}(1-\varepsilon)/[D_{s,i}(Dg_{s,i} + Dg_{p,i}) + D_{p,i}Dg_{p,i}]\varepsilon$
$Bi_{s,i}$	Biot number based on surface diffusivity (dimensionless): $R\ k_{f,i}(1-\varepsilon)/(D_{s,i}\ Dg_{s,i}\ \varepsilon)$
$\overline{C}_i(\overline{t})$	reduced adsorbate concentration in bulk phase as a function of dimensionless time (dimensionless); $C_i(t)/C_{o,i}$
$C_{o,i}$	initial bulk phase concentration (M/L^3)
$\overline{C}_{p,i}(\overline{r},\overline{t})$	reduced adsorbate concentration in adsorbent pores as a function of dimensionless radial position and dimensionless time (dimensionless); $C_{p,i}(r,t)/C_{o,i}$
$C_{p,i}(r,t)$	adsorbate concentration in adsorbent pores as a function of radial position and time (M/L^3)
D_{AA}	self-diffusivity of the adsorbent ($M/L-t$)
Dg_i	combined solute distribution (dimensionless); $(Dg_{s,i} + Dg_{p,i})$
$Dg_{p,i}$	solute distribution parameter based on pore diffusivity (dimensionless); $\varepsilon_p(1-\varepsilon)/\varepsilon$
$Dg_{s,i}$	solute distribution parameter based on surface diffusivity (dimensionless); $\rho_a q_{e,i}(1-\varepsilon)/\varepsilon C_{o,i}$
D_l	liquid diffusivity of the adsorbent (L^2/t)
D_o	dosage of adsorbent (M/L^3)
$D_{p,i}$	pore diffusivity based on pore void fraction (L^2/t)
$D_{s,i}$	surface diffusivity (L^2/t)
$D'_{s,i}$	effective surface diffusivity (L^2/t)
$D_{s,max}$	surface diffusivity of the fastest diffusing component (L^2/t)
F	distribution function (dimensionless)
J_{tot}	total mass flux based on surface and pore diffusion (M/L^2)
k	Boltzmann constant; $1.38054\ 10^{-6}$ erg/°K

K_i	Freundlich isotherm capacity constant $(M/M)(L^3/M)^{1/n}$
$k_{f,i}$	film transfer coefficient (L/t)
M	mass of adsorbent (M)
N_{Re}	Reynolds number; $2\rho_a v_s / \mu$
$N_{Sc,i}$	Schmidt number for component i; $\mu/\rho_a D_{1,i}$
N_o	Avogadro's number; $6.023\ 10^{+23}/mol$
n	number of data points
$1/n_i$	Freundlich isotherm intensity constant (dimensionless)
p	number of parameters
$q_{e,i}$	adsorbent phase concentration in equilibrium with initial bulk phase concentration (M/M); $K_i C_{o,i}^{1/n_i}$
$q_i(r,t)$	adsorbent phase concentration as a function of radial position and time (M/M)
$\bar{q}_i(\bar{r},\bar{t})$	reduced adsorbent phase concentration as a function of dimensionless radial position and dimensionless time (dimensionless); $q_i(r,t)/q_{e,i}$
Q	volumetric flow rate through the differential carbon column (L^3/t)
r	radial coordinate (L)
$\bar{r}$	reduced radial coordinate (dimensionless); r/R
R	adsorbent radius (L)
$S(min)$	minimum relative error (dimensionless)
$S(\Theta)$	relative error for a given confidence contour
St_i	modified Stanton number; $k_{f,i}\ (1 - \varepsilon)\ \tau/\ R\ (\varepsilon)$
T	temperature $(^{\circ}K)$
T_B	boiling point of the adsorbent $(^{\circ}K)$
$\bar{t}_p$	reduced time based on surface and pore diffusion (dimensionless); $[(D_{s,i}/R^2) + (D_{p,i} C_{o,i} \varepsilon_p / R^2 \rho_a Y_{e,i})]t$
$\bar{t}_s$	reduced time based on surface diffusion (dimensionless); $(D_{s,max}/R^2)t$
V	volume of reactor (L^3)

V_b	molar volume of adsorbent (L^3/M)
V_B	volume of the carbon bed; M/ρ_b
v_s	superficial velocity (L/t)
$Y_{e,i}$	total adsorbent phase concentration in equilibrium with initial bulk phase concentration (M/M)
$Y_i(r,t)$	total adsorbent phase concentration as a function of radial position and time (M/M); $q_i(r,t) + \varepsilon_p C_{p,i}(r,t)/\rho_a$
$\bar{Y}_i(\bar{r},\bar{t})$	reduced total adsorbent phase concentration as a function of dimensionless radial position and dimensionless time (dimensionless); $Y_i(r,t)/Y_{e,i}$
X_i	ratio of intraparticle phase mass flux due to surface diffusion to total intraparticle phase mass flux (dimensionless); $D_{s,i}Dg_i/(D_{s,i}Dg_i + D_{p,i}Dg_{p,i})$
Z_i	ratio of mass flux in adsorbent pores due to difference between pore and surface diffusion to total intraparticle phase mass flux (dimensionless); $Dg_{p,i}(D_{p,i} - D_{s,i})/(D_{s,i}Dg_i + D_{p,i}Dg_{p,i})$

GREEK SYMBOLS

α	confidence contour (dimensionless)
ε	porosity of the differential column batch reactor (dimensionless)
ε_p	fraction of volumetric space in adsorbent phase unoccupied by adsorbent (dimensionless)
ρ_a	adsorbent density which includes pore volume (M/L^3)
ρ_b	bulk density of the carbon (M/L^3)
ρ_s	density of graphite which ranges from 2.0 to 2.2 g/cm^3
τ_r	hydraulic retention time (t)
τ	fluid residence time in the packed bed; V_B/Q
τ_p	tortuosity of adsorbent (dimensionless)
μ	viscosity of water (M/L-t)
μ_A	viscosity of adsorbent (M/L-t)

ABBREVIATIONS

BHSDM	Batch Homogeneous Surface Diffusion Model
BPSDM	Batch Pore and Surface Diffusion Model
CMBR	Completely Mixed Batch Reactor
DCBR	Differential Column Batch Reactor
DCE	cis-1,2 Dichloroethene
EB	Ethylbenzene
F-400	Calgon's Filtrasorb 400
GAC	Granular Activated Carbon
IAST	Ideal Adsorbed Solution Theory
IMSL	International Mathematical and Statistical Libraries
PCE	Tetrachloroethene
PGAC	Powdered Granular Activated Carbon
PDFC	Pore Diffusion Flux Contribution
PSDFR	Pore to Suface Diffusion Flux Ratio
SOCS	Synthetic Organic Compounds
TCE	Trichloroethene
TOL	Toluene
VOCS	Volatile Organic Compounds
WV-G	Westvaco's Carbon

APPENDIX 3. TRACE ORGANICS RESEARCH EQUIPMENT CLEANING PROCEDURE

All of the materials that came into contact with either the activated carbon or the volatile organic compounds were cleaned by the trace organics research equipment cleaning procedure. This procedure prevented leaching of volatile organic compounds from the glassware to the carbon.

A. Glassware

1. The glassware was cleaned with MICRO (International Products Corporation, Trenton, N.J.), a laboratory detergent. The soap was a phosphate free laboratory cleaner.
2. All glassware which was used in experiments were chromerged. Chromerge is a trade name for a chromic acid cleaning solution.
3. The cleaned glassware was soaked with the chromerge solution for at least two hours.
4. The chromerge solution was removed and the glassware was thoroughly rinsed with distilled water.
5. The glassware was allowed to air dry. A dilute solution of sulfuric acid (10 parts distilled water : 1 part concentrated sulfuric acid) was used to rinse the glassware. The glassware was soaked with the acid solution for one-half hour.
6. The sulfuric acid solution was removed and the glassware was rinsed with distilled water.
7. The glassware was baked for one hour at 250 °C to remove the water.
8. The glassware was silinized to remove any active sites on the glassware where adsorption could occur. The mixture used

was a 10% solution of dimethyldichlorosilane in toluene.

9. The glassware was soaked in the silane solution for 10 minutes. The glassware was baked at 250°C for one hour.

10. Steps 2 through 9 were conducted every four months on the glassware used in the laboratory.

11. The glassware was rinsed with tap water.

12. The glassware was rinsed with distilled water and allowed to air dry.

13. The glassware was rinsed with technical grade methanol. The glassware was allowed to air dry to evaporate the methanol.

14. The glassware was placed in an oven at 250°C for at least one hour. This helped to drive off any organics that may have been present upon the glassware.

15. The glassware was cooled and covered with aluminum foil, shiny side up.

B. Teflon

1. The teflon was washed with the MICRO detergent.

2. The teflon was rinsed with tap water.

3. The teflon was rinsed with distilled water and allowed to air dry.

4. The teflon was rinsed with technical grade methanol and allowed to air dry.

5. The teflon was baked in a forced air oven at 105°C for one hour.

6. The teflon circles were stored in a clean beaker and covered with aluminum foil, shiny side up.

C. Rubber septa

1. The rubber septa were washed with the MICRO detergent.

2. The rubber septa were rinsed with tap water.

3. The rubber septa were rinsed with distilled water and allowed to air dry.

4. The rubber septa were rinsed with technical grade methanol.

5. The rubber septa were placed in the forced air oven at 105°C for ten minutes.

6. The rubber septa were stored in a clean beaker and covered with aluminum foil, shiny side up.

D. Stainless steel

1. The stainless steel fittings were washed with the MICRO detergent and rinsed with tap water.

2. The stainless steel fittings were rinsed with distilled water and allowed to air dry.

3. The stainless steel fittings were rinsed with technical grade methanol and allowed to air dry.

4. The stainless steel fittings were baked in a forced air oven at 105°C for one hour.

5. The stainless steel fittings were removed from the oven and covered with aluminum foil, shiny side up.

APPENDIX 4. CARBON PREPARATION AND CHARACTERIZATION

A. Procedure for Obtaining a Representative Sample of GAC

In this study, Calgon's Filtrasorb 400 (F-400), (lot number 52095), and Westvaco's WV-G (lot number 39815) granular activated carbons were used. It was important to insure a representative sample of the lot, since shipping and handling could cause attrition and stratification of the carbon in the bag. A sample splitter was used to obtain a uniform sample of carbon.

Prior to splitting the carbon, all of the equipment which came into contact with the carbon was cleaned by the Trace Organics Research Equipment Cleaning Procedure. See Appendix 3.

1. Carbon Splitting Procedure

The carbons were each contained in two 50 pound bags and were split into smaller samples such that a representative sample of the bag could be obtained.

1. The two 50 pound bags were first split by consecutively removing 1 liter of carbon from each bag. This effectively combined the contents of each bag. The bags were labeled 1 and 2.
2. Bag 2 was set aside and bag 1 was split into two lots labeled A and B.
3. Bag B was set aside and bag A was split into two lots labeled C and D.
4. Bag D was set aside and bag C was split into two lots labeled E and F.
5. Bag E was used for equilibrium, kinetic, mini-column, small-column, particle size distribution and bulk density experiments. Bag F was used for the pilot unit which was set up in Wausau,

Wisconsin.

B. Procedure for Washing the GAC

Before the carbon was used for experimentation, it was washed to remove the fine carbon particulates. The presence of the fine carbon particles could cause the adsorption rate to be faster than it would be if only uniform particles were used.

1. Approximately 500 ml of GAC was placed in a 1 liter beaker.
2. 300 ml of Milli-Q water was added into the beaker.
3. The contents were swirled with a glass stirring rod.
4. The contents were allowed to settle for five minutes.
5. The supernatant was decanted and more Milli-Q water was added until the supernatant was clear.
6. The GAC was placed in an oven at 105°C for 16 hours.
7. The carbon was removed and allowed to cool in a dessicator.
8. The carbon was transferred into clean, brown, borosilicate bottles with teflon circles in the caps and stored in a cool place.

C. Procedure to Determine the Particle Size Distribution

A good value of the mean particle size will enable the mathematical models to better describe the data. A particle size distribution was conducted for this purpose.

1. A 500 gm sample of the washed F-400 and WV-G carbons were obtained. Since the carbon was 12x40 mesh, the following U.S. standard mesh sieves were used: 10, 12, 18, 20, 25, 30, and 40.
2. The sieves were stacked in the following order: 10, 12, 18, 20, 25, 30, and 40. The smallest mesh was at the top of the stack and

the largest mesh was at the bottom of the stack.

3. The sieves were placed on a Ro-tap and the 500 gm sample was added.

4. The GAC was agitated on the Ro-tap for 30 minutes.

5. The GAC on each sieve was placed in a clean beaker and the carbon weight was determined.

The raw data for the sieve analysis for both carbons are presented in Table 4-1. Table 4-2 contains the sieve size and sieve openings along with the amount of carbon which passed each sieve. The results are plotted in Figures 4-1 and 4-2 (Fair et. al., 1971). The mean particle diameters for the WV-G and F-400, 12x40 mesh carbons, were 0.1074 cm and 0.1026 cm, respectively. The uniformity coefficients, C_u, for the WV-G and F-400, 12x40 mesh carbons were 1.9 and 1.7, respectively.

D. Procedure to Determine Grain Shape and Shape Variation of the GAC

1. A representative sample of both the WV-G and F-400, 12x40 carbons were obtained.

2. Both carbons were observed under a microscope and compared to Figure 4-3 (Fair et. al., 1971).

The results for the WV-G and F-400 carbons are shown in Figure 4-4. The bed void fractions for the WV-G and F-400 carbons are 0.425 and 0.405, respectively (Kato, 1984).

E. Procedure to Determine the Bulk Density of the GAC

1. A clean, 100 ml, graduated cylinder was obtained for this experiment. A round, porous, glass plate fit tightly in the graduated cylinder.

2. Various amounts of weighed, dry carbon were placed in clean

Table 4-1. Results of the Sieve Analysis for the F-400 and WV-G Carbons.

Standard Sieve Size	WV-G Carbon Weight (gm)	Percent Weight WV-G (%)	F-400 Carbon Weight (gm)	Percent Weight F-400 (%)
10 x 12	11.5	2.34	5.0	1.00
12 x 18	268.0	54.42	285.0	57.11
18 x 20	76.0	15.43	81.0	16.23
20 x 25	47.0	9.54	52.0	10.42
25 x 30	44.0	8.93	39.5	7.92
30 x 40	32.5	6.60	28.5	5.71
> 40	13.5	2.74	8.0	1.61
		100%		100%

Table 4-2. Sieve Size and Percent Carbon Passing a Given Sieve for the F-400 and WV-G Carbons.

Standard Sieve Size	Sieve Opening (cm)	Percent Passed F-400 (%)	Percent Passed WV-G (%)	Log Size (cm)
10	0.200	100.0	100.0	-0.699
12	0.168	99.0	97.7	-0.775
18	0.100	41.9	43.2	-1.000
20	0.084	25.7	27.8	-1.076
25	0.071	11.8	18.2	-1.149
30	0.056	7.3	9.3	-1.125
40	0.042	1.6	2.7	-1.377

Note: The original weight basis was 500 gm for each carbon.

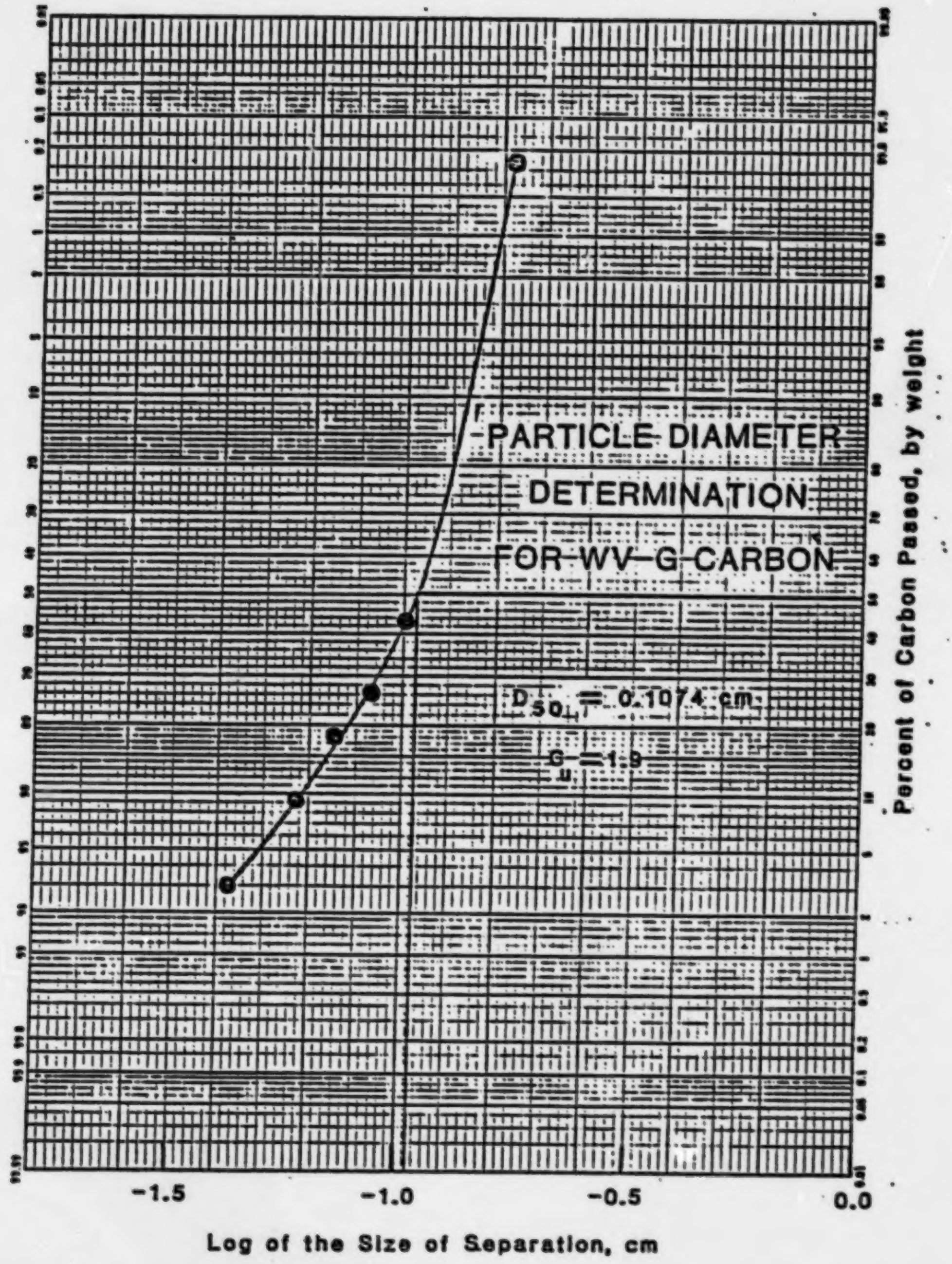


Figure 4-1. Percent Carbon (by weight) Passing a Given Sieve Size Versus the Log of the Size of Separation for WV-G Carbon.

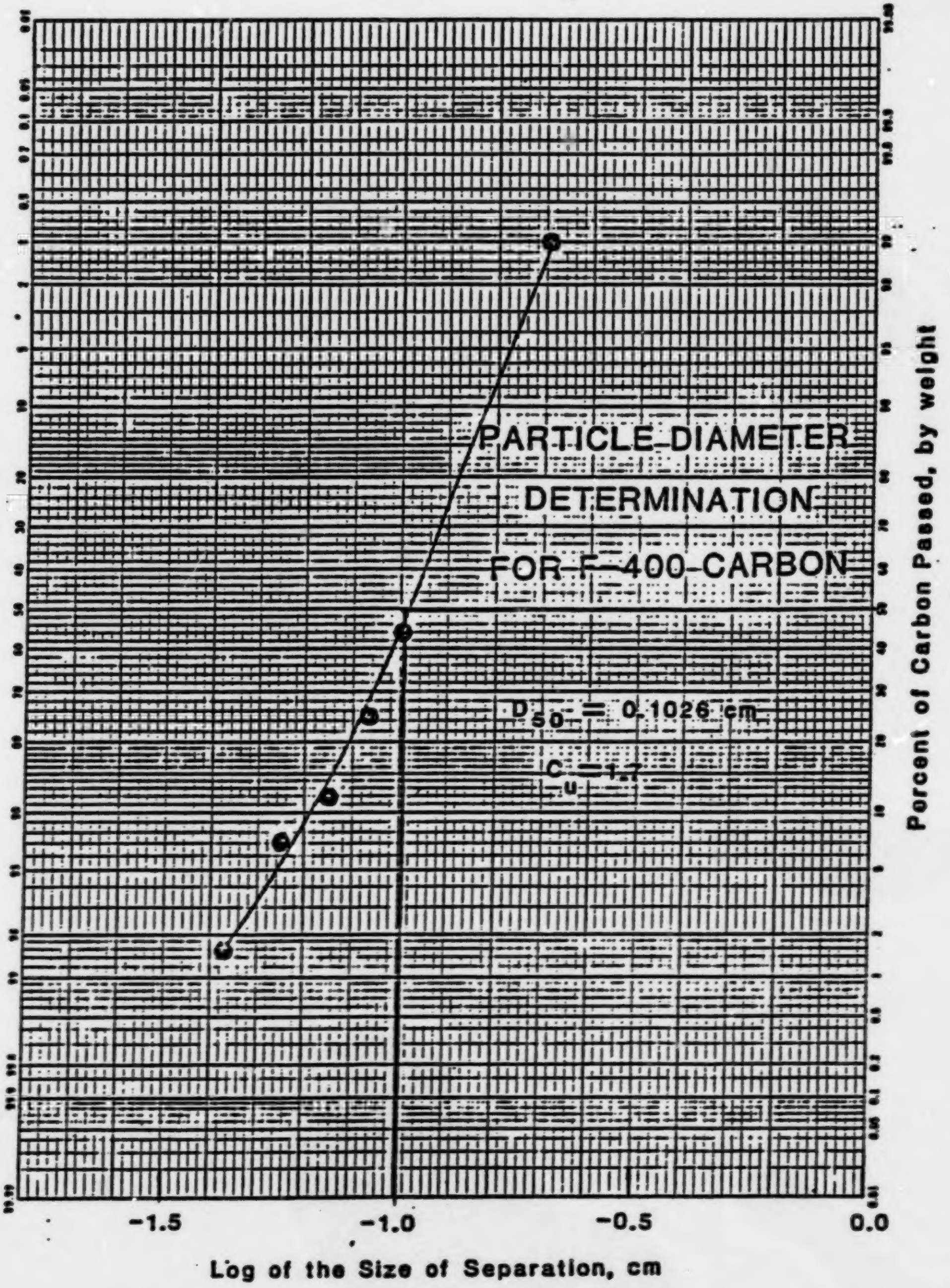


Figure 4-2. Percent Carbon (by weight) Passing a Given Sieve Size Versus the Log of the Size of Separation for F-400 Carbon.

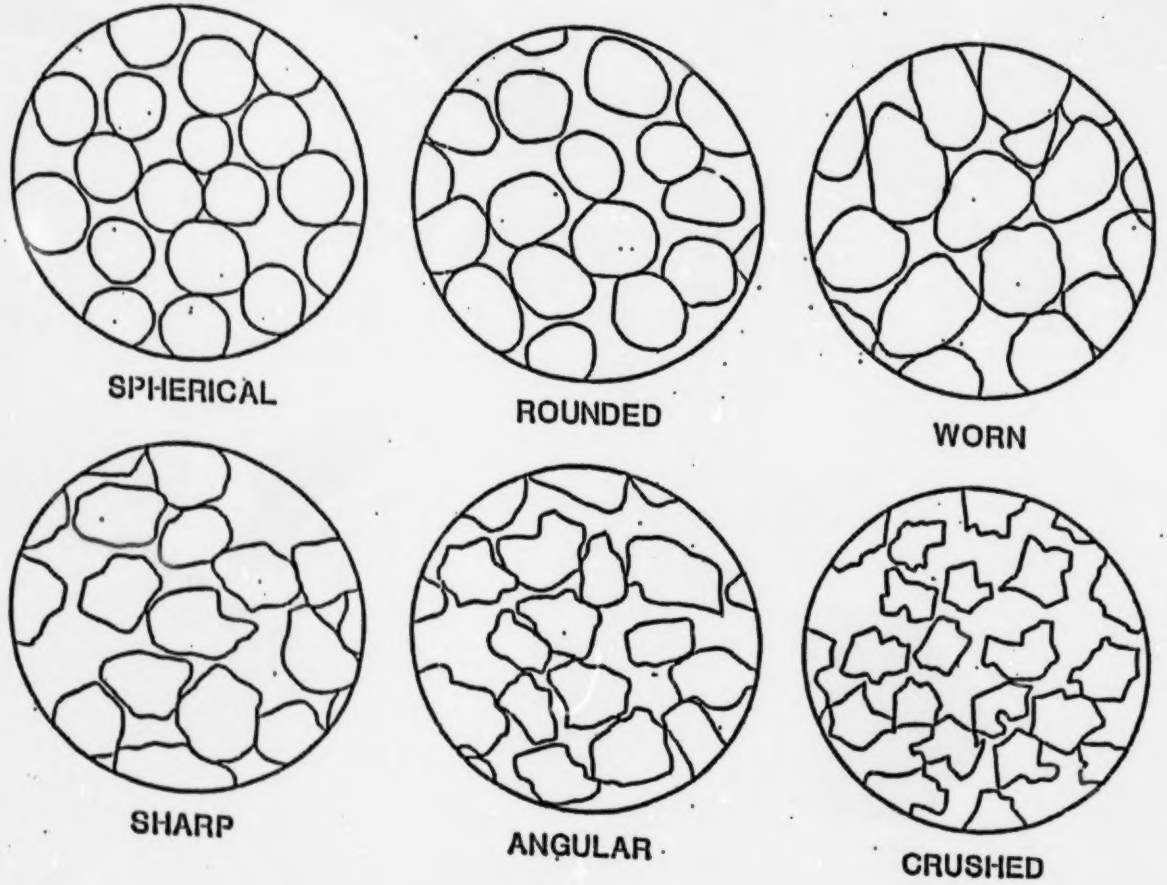


Figure 4-3. Shape Factors of Granular Materials and Typical Porosities Associated with them (Fair et al., 1971).

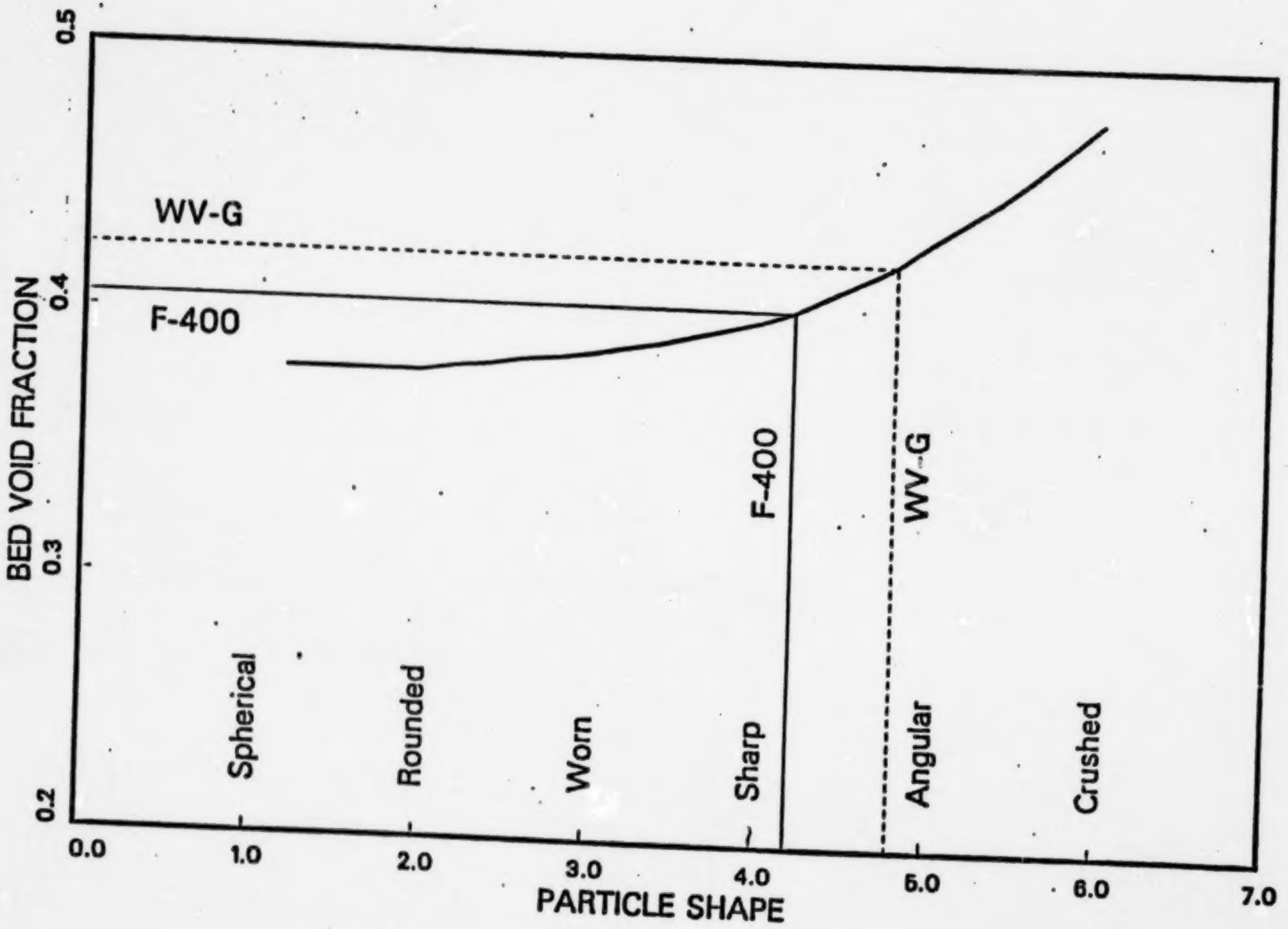


Figure 4-4. Relationship Between the Bed Void Fraction and the Particle Shape.

beakers containing Milli-Q water and allowed to set overnight.

3. A beaker containing the carbon was poured into the graduated cylinder and the carbon was allowed to settle.

4. The round, porous, glass plate was placed on top of the carbon and the volume was recorded.

The size of the graduated cylinder was important in the determination of the bulk density. For the wall effects to be negligible, the diameter of the graduated cylinder should be at least 20 particle diameters. In this case, the graduated cylinder was 25 particle diameters. The data for the bulk density experiment are shown in Table 4-3 (Kato, 1984). Figure 4-5 shows the data plotted using the International Mathematical and Statistical Libraries (IMSL) linear least squares method. The bulk densities for both 12x40 carbons were determined by minimizing the sum of the squares of the percent error in the weight measurements. The equation was of the form, Y=A*X, and the line was forced through zero. The bulk densities for the WV-G and F-400 carbons were 0.433 g/cm^3 and 0.478 g/cm^3, respectively.

F. Calculation of the Apparent Density

The apparent density was calculated using the void fractions and bulk densities from 4-D and 4-E, respectively:

$$\rho_a = \frac{\rho_b}{(1 - \varepsilon)} \qquad (4\text{-}1)$$

The apparent densities for the WV-G and F-400 carbons were 0.7530 g/cm^3 and 0.8034 g/cm^3, respectively.

Table 4-3. Data Collected From the Bulk Density Experiment for 12 x 40 mesh F-400 and WV-G Carbons.

Weight of F-400 Carbon (gm)	Volume of F-400 Carbon (cm^3)	Weight of WV-G Carbon (gm)	Volume of WV-G Carbon (cm^3)
3.76	8.2	2.05	4.8
6.75	14.5	3.97	8.8
9.89	19.9	5.90	13.6
15.61	27.1	8.51	19.5
16.09	33.6	10.91	26.0
19.06	39.7	12.85	29.6
----	----	14.99	34.2

Note: This experiment was conducted with a 100 ml graduated cylinder (Kato, 1984).

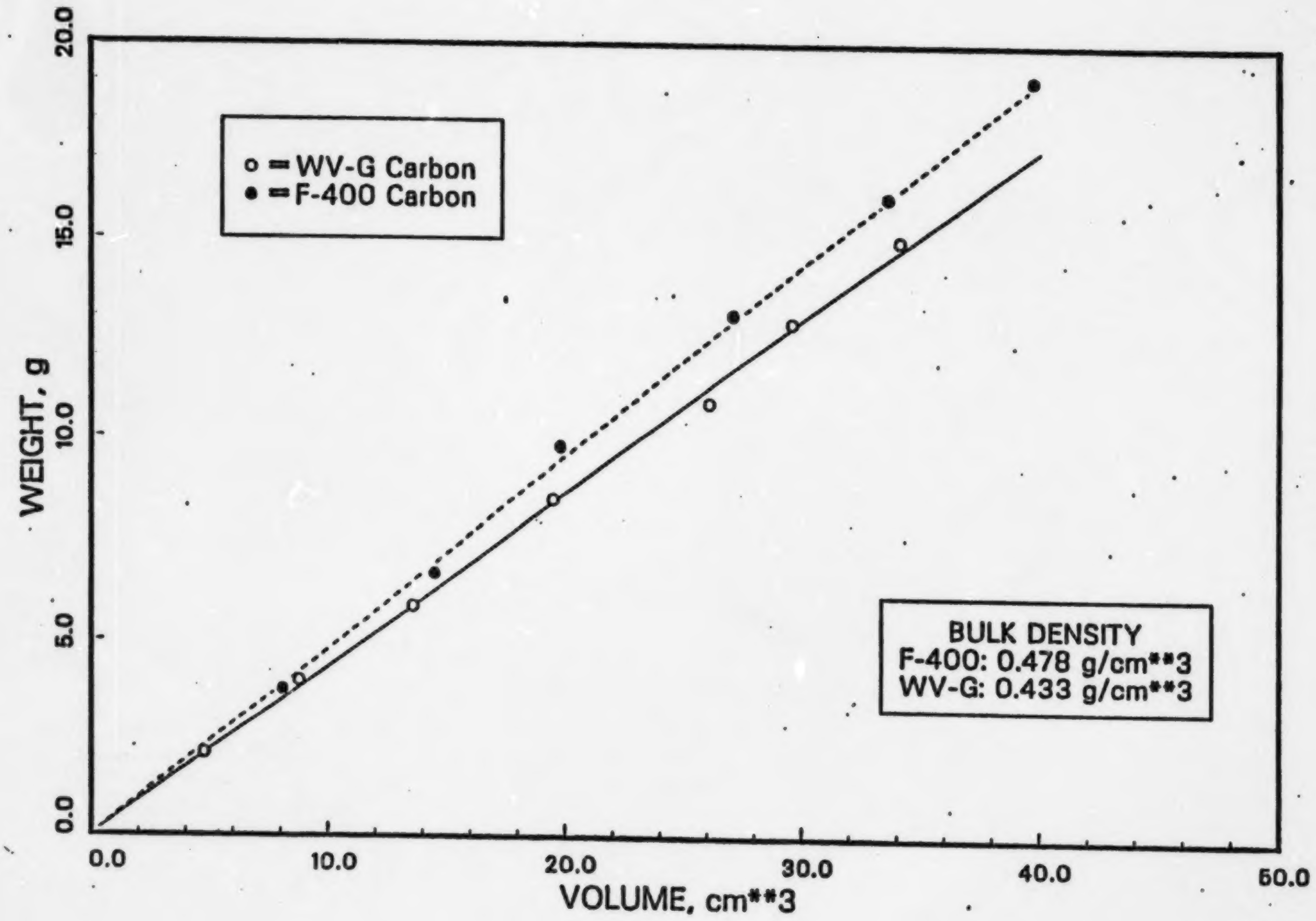


Figure 4-5. Determination of the Bulk Density of F-400 and WV-G Carbons Using a Dry Weight of Carbon Versus the Volume Occupied by Milli-Q Water (Kato, 1984).

G. Calculation of the Intraparticle Void Fraction

The intraparticle void fraction was calculated using the apparent densities from Appendix 4-F and the density of graphite, ρ_g, which is 2.2 g/cm³:

$$\varepsilon_p = 1 - \frac{\rho_a}{\rho_g} \qquad (4-2)$$

The intraparticle void fractions for the WV-G and F-400 carbons were 0.658 g/cm^3 and 0.641 g/cm^3, respectively.

H. Preparation of Powdered and Ground Activated Carbon

The powdered activated carbon (200 x 400 MESH) was used in the bottle point isotherm studies and the ground granular activated carbon (60 x 80 MESH) was used in some of the differential column batch reactor (DCBR) and mini-column studies.

There are two methods to produce either powdered or ground activated carbon: the use of a ball mill or mortar and pestle. The mortar and pestle was employed, since it was the most convenient and available method. The yield from the mortar and pestle for both the powdered and ground carbon was 60%.

1. Procedure for Obtaining Powered and Ground Activated Carbon

a. The mortar and pestle were cleaned according to the procedure presented in Appendix 3.

b. An initial amount of carbon (100 g) was crushed. This carbon was separated using the following sieves: 30, 35, 40, 60, 80, 100, and 200. This was done to observe the amount of carbon which would pass the 60 mesh, but be retained on the 80 mesh.

c. The carbon which was retained on the 80 mesh was set aside and the carbon which did not pass the 60 mesh sieve was further crushed.

d. Steps 2 through 3 were continued until all of the original 100 gm sample had passed the 60 mesh and the desired amount of ground activated carbon was obtained.

e. For Powered Granular Activated carbon, the following sieves were used: 40, 50, 60, 80, 100, 200, and 400. In this case, the carbon must pass the 200 mesh, but be retained on the 400 mesh.

2. Procedure to Clean the Ground and Powdered Activated Carbon

a. The carbon was placed in a centrifuge bottle (250 ml). The bottle was filled about full.

b. Milli-Q water, purged with helium, was added to the centrifuge bottle. The Milli-Q water was purged because trace amounts of chloroform were detected in the Milli-Q system. Care was also observed when the water was added to the dry carbon. The powdered or ground carbon will adsorb water and displace air, causing the carbon to splatter.

c. The centrifuge bottles were placed into the centrifuge and rotated at 2000 RPM for 15 minutes.

d. The bottles were removed and the supernatant was observed.

e. Steps 2 through 4 were continued until the supernatant was clear.

f. The carbon slurry which remained were placed into an oven at 105°C for 16 hours.

g. The carbon was transferred into clean, dark, borosilicate glass bottles with teflon circles in the caps. The bottles were placed in a dessicator for future use.

APPENDIX 5. PROCEDURE FOR DIFFERENTIAL COLUMN BATCH REACTOR

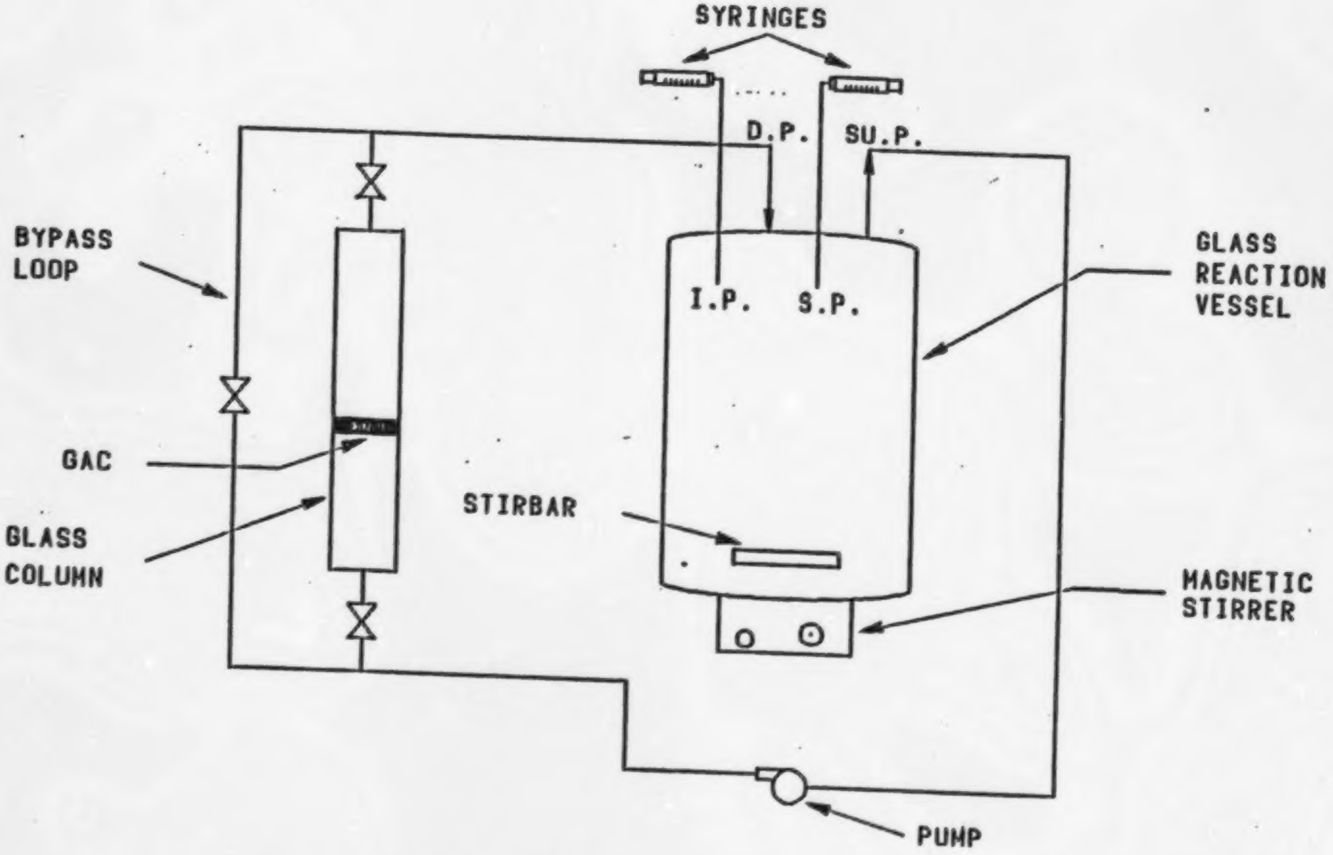
The following procedure was used in the evaluation of the surface diffusivities of various volatile organic compounds (VOCS). Figure 5-1 displays the general design of the differential column batch reactor (DCBR). Table 5-1 contains the equipment list for the DCBR. The unit was constructed using glass, teflon, and stainless steel parts. These materials are chemically inert and reduce the possibility of biased results due to system leaching. The glassware, teflon, and stainless steel appurtances were cleaned according to the Trace Organics Cleaning Procedure, Appendix 2.

A. General Operation of the Differential Column Batch Reactor

1. A continuously mixed glass reaction vessel was completely filled with a water matrix run at isothermal conditions.
2. A pH of 6.0 was controlled using a suitable buffer.
3. The suction line leaving the reactor was connected to a pump. The discharge line can either pass the water through a bypass loop or through a column packed with a differential height of granular activated carbon (GAC). Figure 5-2 describes the suction and discharge port for each reactor design, respectively.

B. Selecting the Proper Column

Various column diameters may be used in the study. The column diameter was chosen, based on the mass of carbon used and on the carbon particle size, to insure a minimum of channeling and wall effects.



D.P. - DISCHARGE PORT
I.P. - INJECTION PORT
SU.P. - SUCTION PORT
S.P. - SAMPLING PORT

⧖ - WHITEY REGULATING VALVE

Figure 5-1. Basic Design for the Differential Column Batch Reactor.

Table 5-1. Equipment List for the Differential Column Batch Reactor

1-F.M.I. Pump, Model RP, 1/4 Inch Piston
1-12L Glass Carboy Reactor
1-Fisher Scientific Stirplate
3-3/8 Inch Whitey Regulating Valves, (SS)
3-3/8 Inch Swagelok Union Tee, (SS)
5-3/8 Inch Swagelok Union Elbows, (SS)
2-3/8 Inch to 1/4 Inch Swagelok Reducing Union, (SS)
2-3/8 Inch to 3/8 NPT Swagelok Male Connector, (SS)
2-Hamilton 4-Port Valve
1-5 ml Hamilton Syringe With Luer-Loc
1-30 ml Hamilton Syringe With Luer-Loc
1-50 ml Hamilton Syringe With Luer-Loc
1-1 Inch Teflon Stirbar
1-#12 Rubber Stopper
2-Teflon End Plugs, #15
100gm, 3mm Diameter Glass Beads
Silanized Glass Wool

Glass Columns:
6,11,15,25mm

Tubing:
3/8 Inch Teflon For Main Lines
1/8 Inch Teflon for sampling and Injection Lines

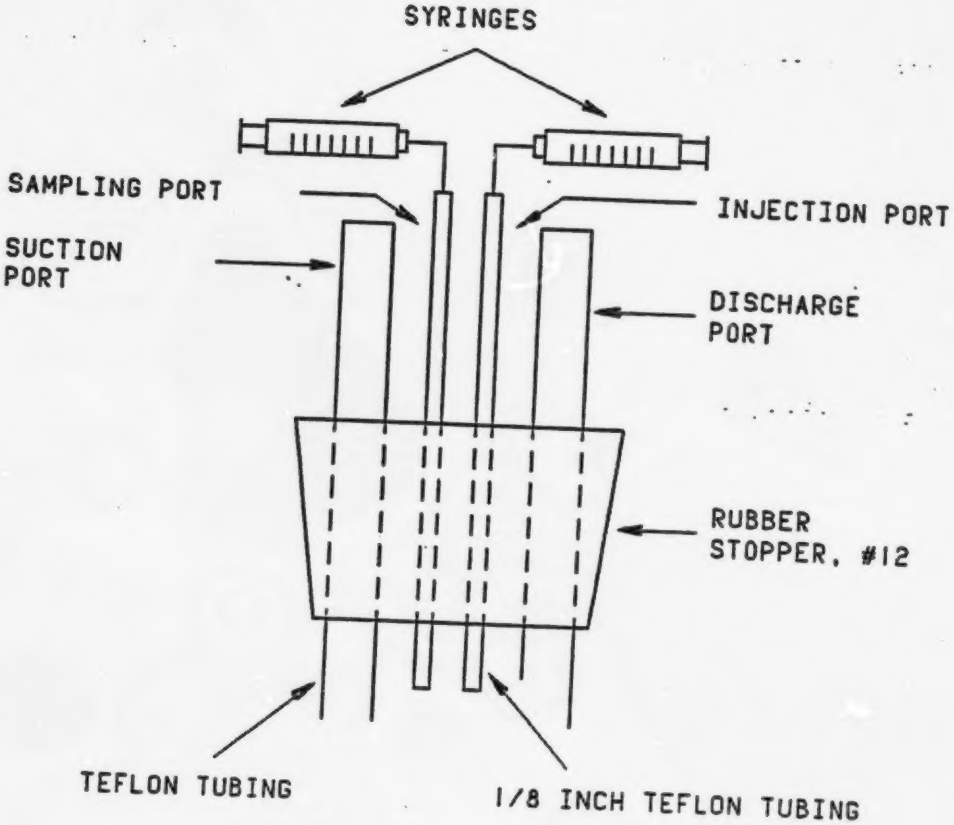


Figure 5-2. Schematic of the Ports for the Differential Column Batch Reactor.

C. Selecting the Proper Carbon Dosage

To the extent possible, the mass of carbon used in a rate study should reduce the concentration of a VOC by at least 50% of the initial concentration to obtain good rate data Hand et. al., 1983).

To calculate the carbon dosage, D_o, an overall mass balance for component i in the DCBR may be written in word form as:

$$\begin{matrix}\text{Mass of Component i} & & \text{Mass of Component i} & & \text{Mass of Component i} \\ \text{in the DCBR} & = & \text{in the Liquid Phase} & + & \text{in the solid phase} \\ \text{Initially} & & \text{at Equilibrium} & & \text{at Equilibrium}\end{matrix}$$

In mathematical terms this is expressed as:

$$C_{o,i} = C_{e,i} + \frac{M\, q_{e,i}}{V} \qquad (5-1)$$

Substituting the Freundlich isotherm equation into equation 5-1 yields:

$$D_o = \frac{M}{V} = \frac{(C_{o,i} - C_{e,i})}{K_{,i}\, C_{e,i}^{1/n_i}} \qquad (5-2)$$

in which, M is the mass of adsorbent, gm, V is the volume of the DCBR, cm^3, $C_{o,i}$ is the initial concentration of component i, μmol/L, $C_{e,i}$ is the equilibrium concentration of component i, μmol/L, K is the Freundlich isotherm constant, μmol/g $(L/\mu mol)^{1/n_i}$, and $1/n_i$ is the Freundlich isotherm constant, (dimensionless).

D. Packing the Differential Carbon Column

Figure 5-3 displays the packed column. Teflon end caps were packed with silianized glass wool to contain the 3.0 mm glass beads. The carbon was packed between a bed of silanized glass wool.

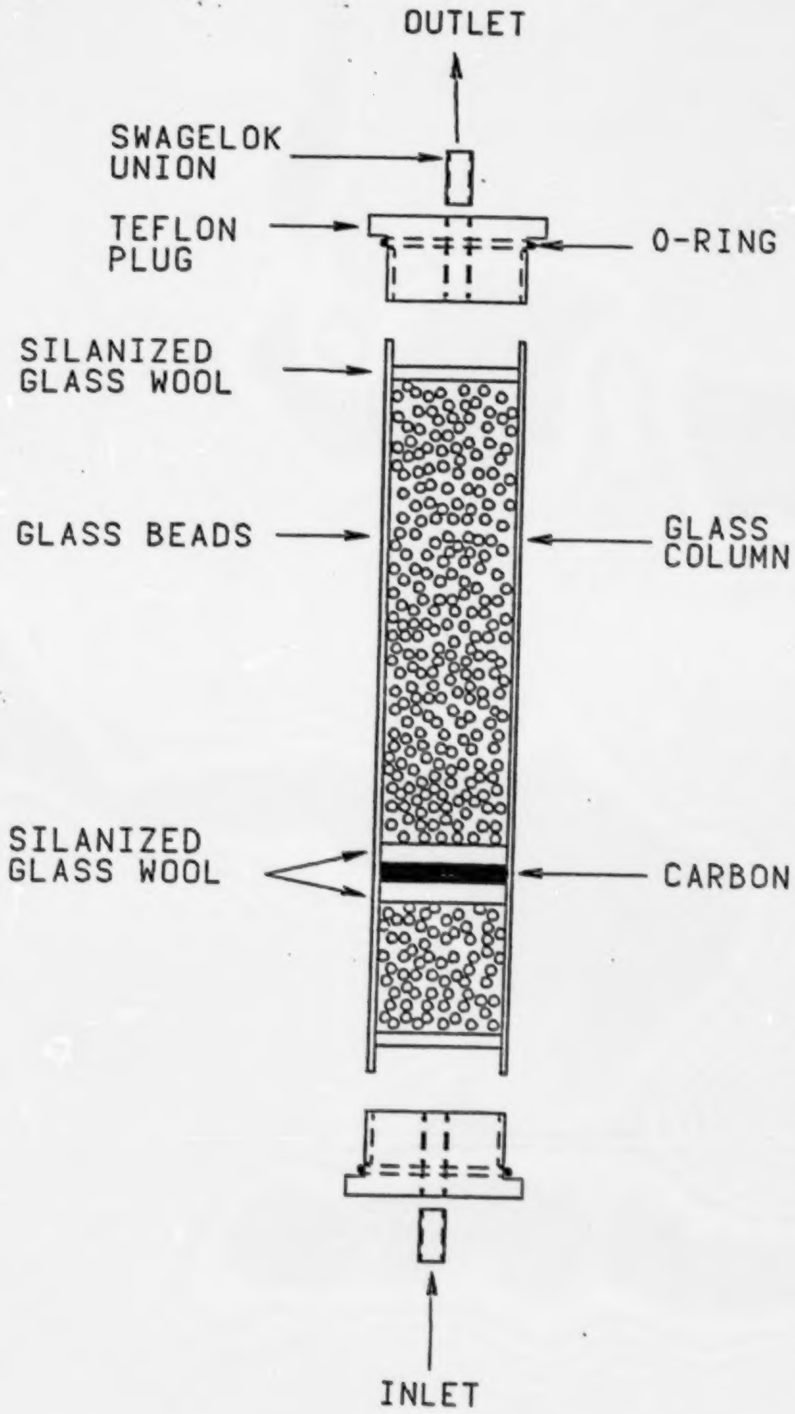


Figure 5-3. Schematic of the Packed Differential Carbon Column.

E. Measuring the flow rate of the DCBR

The flow rate to the DCBR was an important consideration in the determination of the surface diffusivity. See Section V-A for further discussion. A high flow rate was required to obtain a good estimate of the surface diffusivity. The hydraulic retention time is the ratio of the the reactor volume to the flow rate (See Equation V-1). This indicated the frequency at which samples could be taken. The flow rate was measured by packing the column with 3.0 mm glass beads and collecting the water over an elapsed time period.

F. Spiking the Reactor with a VOC

1. When the batch reactor system showed no sign of leakage, the water matrix was spiked with a VOC.
2. A concentrated stock solution of the desired organic chemical was prepared in methanol.
3. The stock solution was injected into the reactor and Milli-Q water was displaced. This allowed for no headspace in the system.
4. The system was run with the bypass loop open until a steady-state concentration was realized.
5. Elapsed time for the batch test started when the bypass loop was closed and the water began to flow through the column.

G. Sampling from the Differential Column Batch Reactor

Samples were analyzed using either the liquid-liquid extraction or the purge and trap technique. See Section II-E for further discussion. The techniques used to remove a sample for analysis are presented below.

1. Sampling for the Liquid-Liquid Extraction Technique

a.) The 25 ml sample bottles with teflon circles, rubber septa, and tear-off aluminum seals (Wheaton Scientific, Millville, N.J.) were tared.

b.) The extraction ratio was calculated (Johnson, 1984) and the appropriate volume of isooctane was added to the 25 ml bottle.

c.) The bottle was weighed again to determine the amount of isooctane added.

d.) Samples were taken with a 5 ml syringe by displacement with a 30 ml syringe filled with an unspiked water matrix.

e.) To insure a representative sample was taken at an elapsed time, a 1 ml sample was removed, since there was dead volume in the sample line. Figure 5-4 describes the design of the sampling and injection ports for the DCBR.

f.) The water sample was injected below the isooctane phase so volatilization would be minimized.

g.) The bottle was re-weighed and the mass recorded. The volume of the isooctane and water were calculated by using the densities. An extraction ratio was also calculated.

h.) Collection of the samples were continued until the organic saturated the GAC.

2. Sampling for the Purge and Trap Technique

a.) A 25 ml extraction bottle with a teflon circle, rubber septa, and aluminum seal were used.

b.) Samples were taken with a 30 ml syringe by displacement with a 50 ml syringe filled with an unspiked water matrix.

c.) To insure a representative sample at a given elapsed time, a 1

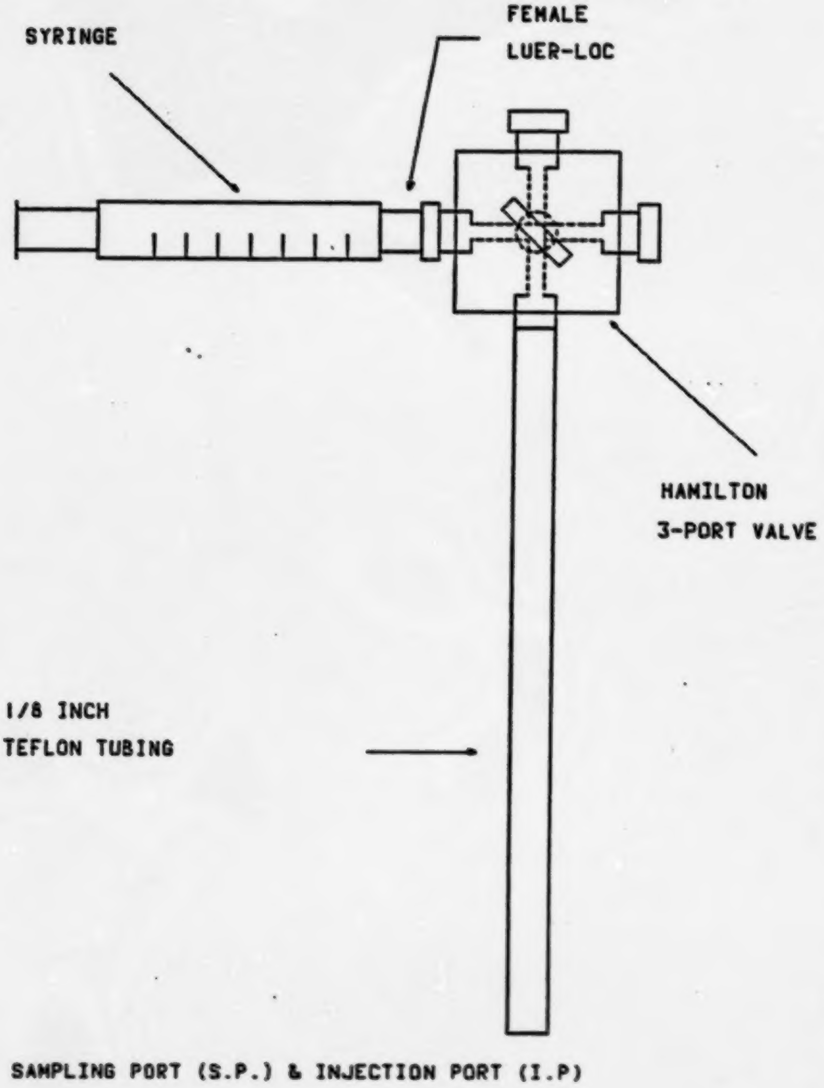


Figure 5-4. Design of the Sampling and Injection Ports for the Differential Column Batch Reactor.

ml sample was removed, since there was dead volume in the sampling line.

d.) The aqueous sample was added to the the 25 ml bottle allowing for no headspace.

e.) Collection of samples are continued until the organic saturated the GAC.

APPENDIX 6. DIFFERENTIAL COLUMN BATCH REACTOR DATA

Table 6-1. Batch Kinetic Data for Trichloroethene and (12x40) F-400 Carbon Using Thawed Wausau Water.

PARAMETERS:

Volume of Reactor: 4975 cm^3

Initial Concentration: 1441.6 µg/L

Particle Radius: 0.05129 cm

Particle Density: 0.8034 g/cm^3

Column Diameter: 1.10 cm

Freundlich Intensity Constant: 0.4165

Freundlich Capacity Constant: 196.6 $\mu\text{m/g}(\text{L}/\mu\text{m})^{1/n}$

Weight of Carbon Used: 0.30185 g

Best Fit Surface Diffusion Coefficient Using BHSDM: $2.60\ 10^{-10}\ \text{cm}^2/\text{s}$

Calculated Film Transfer Coefficient Using Fixed Bed Correlation: $1.50\ 10^{-2}$ cm/s

Best Fit Film Transfer Coefficient Using BHSDM: $1.50\ 10^{-2}$ cm/s

95% Confidence Interval For Surface Diffusion Coefficient: $2.35\text{-}2.95\ 10^{-10}\ \text{cm}^2/\text{s}$

Solute Distribution Factor: 2.9474

Biot Number: 75.82

Stanton Number: 0.0085

Reactor Porosity: 0.99992

Temperature of Reactor: 11.0 °C

Superficial Velocity: 14.46 cm/s

Hydraulic Retention Time: 6.03 min

pH of Water Matrix: 6.93

Table 6-1 (Continued).

Initial Concentration: 1441.7 µg/L
Carbon Type: F-400 (12x40) MESH
Water Matrix: Thawed Wausau Water

Elapsed Time (minutes)	Experimental Concentration (µg/L)
150.0	1032.3
210.0	952.8
270.0	886.3
330.0	849.1
395.0	814.4
450.0	772.0
525.0	732.0
1185.0	610.0
1260.0	543.1
1355.0	521.4
1425.0	500.0
1520.0	488.5
1600.0	471.3
1815.0	450.0
1920.0	439.0
2495.0	405.6
2610.0	386.5
2790.0	360.2
2970.0	343.1
3165.0	350.5
3330.0	333.6
3645.0	327.8
4055.0	314.5
4245.0	306.3
4410.0	296.8
4600.0	286.0
5505.0	293.9
5745.0	272.0
6040.0	250.2
6150.0	254.6
6905.0	264.7
6990.0	249.9
7110.0	244.1
7290.0	242.8
7530.0	241.3
7650.0	239.7
7770.0	236.5
8370.0	241.1
8490.0	237.8

Table 6-2. Batch Kinetic Data for Trichloroethene and (12x40) WV-G Carbon Using Thawed Wausau Water.

PARAMETERS:

Volume of Reactor: 4920 cm^3

Initial Concentration: 1241.6 µg/L

Particle Radius: 0.05370 cm

Particle Density: 0.7530 g/cm^3

Column Diameter: 1.10 cm

Freundlich Intensity Constant: 0.4073

Freundlich Capacity Constant: 181.0 $\mu m/g(L/\mu m)^{1/n}$

Weight of Carbon Used: 0.30304 g

Best Fit Surface Diffusion Coefficient Using BHSDM: 2.8 10^{-10} cm^2/s

Calculated Film Transfer Coefficient Using Fixed Bed Correlation: 1.54 10^{-2} cm/s

Best Fit Film Transfer Coefficient Using BHSDM: 1.54 10^{-2} cm/s

95% Confidence Interval For Surface Diffusion Coefficient: 2.4-3.25 10^{-10} cm^2/s

Solute Distribution Factor: 2.9450

Biot Number: 82.03

Stanton Number: 0.0077

Reactor Porosity: 0.99992

Temperature of Reactor: 11.0 °C

Superficial Velocity: 15.38 cm/s

Hydraulic Retention Time: 5.61 min

pH of Water Matrix: 6.93

Table 6-2 (Continued).

Initial Concentration: 1241.6 μg/L
Carbon Type: WV-G (12x40) MESH
Water Matrix: Thawed Wausau Water

Elapsed Time (minutes)	Experimental Concentration (μg/L)
75.0	1073.6
135.0	992.5
195.0	786.0
255.0	773.3
315.0	743.1
375.0	700.6
760.0	663.0
840.0	579.6
930.0	533.3
1050.0	508.6
1110.0	471.7
1260.0	432.8
1320.0	419.9
1395.0	411.6
1445.0	400.6
1560.0	367.0
1635.0	382.6
2370.0	366.3
2470.0	348.8
2535.0	317.8
2630.0	323.1
2710.0	313.8
2925.0	336.7
3030.0	324.2
3605.0	369.6
3720.0	319.5
3900.0	306.3
4080.0	282.4
4275.0	297.8
4440.0	274.6
4755.0	289.6
5165.0	302.0
5355.0	285.7
5520.0	264.1
5710.0	260.9
5910.0	254.6
6855.0	235.0
6965.0	210.6
7150.0	215.0
7260.0	215.4
7365.0	208.4

Table 6-3. Batch Kinetic Data for Trichloroethene and (12x40) F-400 Carbon Using Milli-Q Water.

PARAMETERS:

Volume of Reactor:	4970 cm^3
Initial Concentration:	1322.7 μg/L
Particle Radius:	0.05129 cm
Particle Density:	0.8034 g/cm^3
Column Diameter:	1.10 cm
Freundlich Intensity Constant:	0.4165
Freundlich Capacity Constant:	196.6 $\mu m/g(L/\mu m)^{1/n}$
Weight of Carbon Used:	0.27587 g
Best Fit Surface Diffusion Coefficient Using BHSDM:	3.1 10^{-10} cm^2/s
Calculated Film Transfer Coefficient Using Fixed Bed Correlation:	2.5 10^{-3} cm/s
Best Fit Film Transfer Coefficient Using BHSDM:	4.51 10^{-3} cm/s
95% Confidence Interval For Surface Diffusion Coefficient:	2.55-3.8 10^{-10} cm^2/s
95% Confidence Interval For Film Transfer Coefficient:	2.75-10.0 10^{-3} cm/s
Solute Distribution Factor:	2.8359
Biot Number:	18.14
Stanton Number:	0.0316
Reactor Porosity:	0.99993
Temperature of Reactor:	11.0 °C
Superficial Velocity:	1.01 cm/s
Hydraulic Retention Time:	85.7 min
pH of Water Matrix Using 10^{-3} M Phosphate Buffer:	6.0

Table 6-3 (Continued).

Initial Concentration: 1322.7 µg/L
Carbon Type: F-400 (12x40) MESH
Water Matrix: Milli-Q

Elapsed Time (minutes)	Experimental Concentration (µg/L)
30.0	1319.3
120.0	1141.6
210.0	1170.0
240.0	1047.4
300.0	1097.6
360.0	1048.0
420.0	913.8
1110.0	700.0
1230.0	668.7
1350.0	628.1
1470.0	661.0
1590.0	571.1
1710.0	541.8
1950.0	433.0
2520.0	442.1
2670.0	460.1
2880.0	402.1
3150.0	377.6
3270.0	351.6
4050.0	352.1
4110.0	319.5
4230.0	293.9
4380.0	299.3
4440.0	287.3
4710.0	283.5
5490.0	275.3
5670.0	247.1
5790.0	225.9
6045.0	213.4
6165.0	212.2
6990.0	220.0
7275.0	206.5
7665.0	224.6

Table 6-4. Batch Kinetic Data for Tetrachloroethene and (12x40) F-400Carbon Using Milli-Q Water.

PARAMETERS:

Volume of Reactor:	4735 cm^3
Initial Concentration:	1438.4 μg/L
Particle Radius:	0.05129 cm
Particle Density:	0.8034 g/cm^3
Column Diameter:	0.6 cm
Freundlich Intensity Constant:	0.4579
Freundlich Capacity Constant:	650.6 $\mu m/g(L/\mu m)^{1/n}$
Weight of Carbon Used:	0.10072 g
Best Fit Surface Diffusion Coefficient Using BHSDM:	4.8 10^{-11} cm^2/s
Calculated Film Transfer Coefficient Using Fixed Bed Correlation:	6.03 10^{-3} cm/s
Best Fit Film Transfer Coefficient Using BHSDM:	7.10 10^{-3} cm/s
95% Confidence Interval For Surface Diffusion Coefficient:	3.5-6.5 10^{-11} cm^2/s
95% Confidence Interval For Film Transfer Coefficient:	4.25-100.0 10^{-3} cm/s
Solute Distribution Factor:	4.2896
Biot Number:	46.81
Stanton Number:	0.0202
Reactor Porosity:	0.99997
Temperature of Reactor:	11.0 °C
Superficial Velocity:	3.44 cm/s
Hydraulic Retention Time:	81.19 min
pH of Water Matrix Using 10^{-3} M Phosphate Buffer:	6.0

Table 6-4 (Continued).

Initial Concentration: 1438.4 μg/L
Carbon Type: F-400 (12x40) MESH
Water Matrix: Milli-Q

Elapsed Time (minutes)	Experimental Concentration (μg/L)
60.0	1421.0
170.0	1386.9
290.0	1336.9
410.0	1298.1
510.0	1299.3
600.0	1193.1
690.0	1208.1
1275.0	935.6
1380.0	883.0
1625.0	868.6
1740.0	824.3
1845.0	823.7
2055.0	775.0
2100.0	745.5
2720.0	684.3
2880.0	691.9
3000.0	706.9
3060.0	657.1
3190.0	673.5
3375.0	677.8
3450.0	520.9
4125.0	561.7
4245.0	579.5
4365.0	567.9
4510.0	608.4
4650.0	597.4
4860.0	550.0
4920.0	548.7
5010.0	555.8
5840.0	460.0
6135.0	458.0
7320.0	416.6
7650.0	392.5
8805.0	430.0
9040.0	420.0
10080.0	376.4
11895.0	338.2

Table 6-5. Batch Kinetic Data for Trichloroethene and (60x80) F-400 Carbon Using Milli-Q Water.

PARAMETERS:

Volume of Reactor: 4975 cm^3

Initial Concentration: 1329.8 µg/L

Particle Radius: 0.01050 cm

Particle Density: 0.8034 g/cm^3

Column Diameter: 1.10 cm

Freundlich Intensity Constant: 0.4165

Freundlich Capacity Constant: 196.6 µm/g(L/µm)$^{1/n}$

Weight of Carbon Used: 0.2220 g

Best Fit Surface Diffusion Coefficient Using BHSDM: 4.3 10^{-10} cm^2/s

Calculated Film Transfer Coefficient Using Fixed Bed Correlation: 2.89 10^{-2} cm/s

Best Fit Film Transfer Coefficient Using BHSDM: 1.4 10^{-2} cm/s

95% Confidence Interval For Surface Diffusion Coefficient: 3.0-8.5 10^{-10} cm^2/s

95% Confidence Interval For Film Transfer Coefficient: 0.9-3.5 10^{-3} cm/s

Solute Distribution Factor: 2.2719

Biot Number: 8.37

Stanton Number: 0.029

Reactor Porosity: 0.99994

Temperature of Reactor: 11.0 °C

Superficial Velocity: 14.46 cm/s

Hydraulic Retention Time: 6.03 min

pH of Water Matrix Using 10^{-3} M Phosphate Buffer: 6.2

Table 6-5 (Continued).

Initial Concentration: 1329.8 μg/L
Carbon Type: F-400 (60x80) MESH
Water Matrix: Milli-Q

Elapsed Time (minutes)	Experimental Concentration (μg/L)
5.0	1273.3
10.0	1005.9
30.0	1076.6
60.0	830.0
90.0	636.1
110.0	684.8
130.0	480.9
150.0	429.2
170.0	378.4
190.0	394.3
225.0	455.0
300.0	279.0
325.0	252.7
350.0	236.5
380.0	222.2
405.0	255.6
455.0	204.6
475.0	200.0
500.0	182.9
525.0	174.7
550.0	171.5
600.0	172.1
700.0	182.9
750.0	195.5
800.0	168.7
850.0	161.6
900.0	167.3
1005.0	153.9
1100.0	163.1

Table 6-6. Batch Kinetic Data for Tetrachloroethene and (60x80) F-400 Carbon Using Milli-Q Water.

PARAMETERS:

Volume of Reactor:	13240 cm^3
Initial Concentration:	1504.0 μg/L
Particle Radius:	0.01050 cm
Particle Density:	0.8034 g/cm^3
Column Diameter:	1.10 cm
Freundlich Intensity Constant:	0.4579
Freundlich Capacity Constant:	650.6 $\mu m/g(L/\mu m)^{1/n}$
Weight of Carbon Used:	0.1720 g
Best Fit Surface Diffusion Coefficient Using BHSDM:	1.5 10^{-10} cm^2/s
Calculated Film Transfer Coefficient Using Fixed Bed Correlation:	2.08 10^{-2} cm/s
Best Fit Film Transfer Coefficient Using BHSDM:	4.3 10^{-2} cm/s
95% Confidence Interval For Surface Diffusion Coefficient:	1.25-1.8 10^{-10} cm^2/s
95% Confidence Interval For Film Transfer Coefficient:	3.25-9.0 10^{-2} cm/s
Solute Distribution Factor:	2.5573
Biot Number:	19.07
Stanton Number:	0.038
Reactor Porosity:	0.99998
Temperature of Reactor:	11.0 °C
Superficial Velocity:	9.61 cm/s
Hydraulic Retention Time:	24.12 min
pH of Water Matrix Using 10^{-3} M Phosphate Buffer:	5.95

Table 6-6 (Continued).

Initial Concentration: 1504.0 µg/L
Carbon Type: F-400 (60x80) MESH
Water Matrix: Milli-Q

Elapsed Time (minutes)	Experimental Concentration (µg/L)
10.0	1457.6
20.0	1318.9
30.0	1144.4
40.0	1136.7
50.0	1034.2
60.0	931.7
70.0	927.3
80.0	978.7
100.0	826.5
110.0	802.0
120.0	754.5
140.0	738.6
160.0	699.6
200.0	591.8
240.0	533.5
270.0	516.7
300.0	467.3
330.0	465.1
420.0	378.9
480.0	351.9
540.0	380.4
600.0	300.0
720.0	287.0
840.0	242.0
960.0	233.0
1080.0	221.6
1200.0	210.7
1320.0	214.1
1440.0	221.2

Table 6-7. Batch Kinetic Data for Trichloroethene and (12x40) WV-G Carbon Using Milli-Q Water.

PARAMETERS:

Volume of Reactor:	4970 cm^3
Initial Concentration:	1318.6 µg/L
Particle Radius:	0.05370 cm
Particle Density:	0.8034 9/cm^3
Column Diameter:	1.10 cm
Freundlich Intensity Constant:	0.4073
Freundlich Capacity Constant:	181.0 µm/g(L/µm)$^{1/n}$
Weight of Carbon Used:	0.27840 g
Best Fit Surface Diffusion Coefficient Using BHSDM:	3.3 10^{-10} cm^2/s
Calculated Film Transfer Coefficient Using Fixed Bed Correlation:	3.10 10^{-3} cm/s
Best Fit Film Transfer Coefficient Using BHSDM:	3.10 10^{-3} cm/s
95% Confidence Interval For Surface Diffusion Coefficient:	2.5-4.7 10^{-10} cm^2/s
Solute Distribution Factor:	2.5828
Biot Number:	14.515
Stanton Number:	0.02050
Reactor Porosity:	0.99993
Temperature of Reactor:	11.0 °C
Superficial Velocity:	1.03 cm/s
Hydraulic Retention Time:	85.7 min
pH of Water Matrix Using 10^{-3} M Phosphate Buffer:	6.0

Table 6-7 (Continued).

Initial Concentration: 1318.6 μg/L
Carbon Type: WV-G (12x40) MESH
Water Matrix: Milli-Q

Elapsed Time (minutes)	Experimental Concentration (μg/L)
30.0	1271.8
90.0	1265.8
120.0	1175.6
180.0	1110.7
240.0	1054.7
300.0	932.4
360.0	909.3
420.0	857.6
510.0	802.9
1320.0	642.3
1440.0	555.8
1560.0	484.2
1860.0	461.3
1950.0	444.8
2820.0	394.6
3240.0	346.9
4320.0	346.6
4620.0	324.2
5670.0	323.1
6120.0	284.7
7260.0	274.6
7680.0	255.1
8490.0	235.4
9000.0	227.5
10410.0	215.5
11610.0	217.2
13410.0	234.3
14430.0	207.5
16140.0	198.5
17460.0	190.7

Table 6-8. Batch Kinetic Data for cis-1,2 dichloroethene and (12x40) F-400 Carbon Using Milli-Q Water.

PARAMETERS:

Volume of Reactor:	13050 cm^3
Initial Concentration:	507.0 μg/L
Particle Radius:	0.05129 cm
Particle Density:	0.8034 9/cm^3
Column Diameter:	1.10 cm
Freundlich Intensity Constant:	0.5616
Freundlich Capacity Constant:	51.0 μm/g(L/μm)$^{1/n}$
Weight of Carbon Used:	0.4537 g
Best Fit Surface Diffusion Coefficient Using BHSDM:	2.7 10^{-9} cm^2/s
Calculated Film Transfer Coefficient Using Fixed Bed Correlation:	1.53 10^{-2} cm/s
Best Fit Film Transfer Coefficient Using BHSDM:	3.00 10^{-2} cm/s
95% Confidence Interval For Surface Diffusion Coefficient:	1.7-5.1 10^{-9} cm^2/s
95% Confidence Interval For Film Transfer Coefficient:	.85-100 10^{-2} cm/s
Solute Distribution Factor:	0.85881
Biot Number:	28.72
Stanton Number:	0.02660
Reactor Porosity:	0.99996
Temperature of Reactor:	12.0 °C
Superficial Velocity:	12.1 cm/s
Hydraulic Retention Time:	19.0 min
pH of Water Matrix:	6.3

Table 6-8 (Continued).

Initial Concentration: 507.0 µg/L
Carbon Type: F-400 (12x40) MESH
Water Matrix: Milli-Q

Elapsed Time (minutes)	Experimental Concentration (µg/L)
30.0	460.7
90.0	430.6
120.0	442.9
180.0	433.4
240.0	391.9
300.0	387.2
360.0	343.6
660.0	272.8
720.0	297.7
1335.0	312.9
1675.0	263.1
2040.0	257.7
2910.0	268.8
3180.0	278.2
4410.0	228.5
4870.0	226.0
6095.0	225.0

Table 6-9. Batch Kinetic Data for Toluene and (12x40) F-400 Carbon Using Milli-Q Water.

PARAMETERS:

Volume of Reactor:	13160 cm^3
Initial Concentration:	373.4 µg/L
Particle Radius:	0.05129 cm
Particle Density:	0.8034 9/cm^3
Column Diameter:	1.10 cm
Freundlich Intensity Constant:	0.3282
Freundlich Capacity Constant:	475.0 µm/g(L/µm)$^{1/n}$
Weight of Carbon Used:	0.1000 g
Best Fit Surface Diffusion Coefficient Using BHSDM:	1.8 10^{-9} cm^2/s
Calculated Film Transfer Coefficient Using Fixed Bed Correlation:	1.48 10^{-2} cm/s
Best Fit Film Transfer Coefficient Using BHSDM:	0.7 10^{-1} cm/s
95% Confidence Interval For Surface Diffusion Coefficient:	1.50-2.25 10^{-9}cm^2/s
Solute Distribution Factor:	1.4111
Biot Number:	133.5
Stanton Number:	0.0134
Reactor Porosity:	0.99999
Temperature of Reactor:	13.0 °C
Superficial Velocity:	14.02 cm/s
Hydraulic Retention Time:	16.45 min
pH of Water Matrix:	6.3

Table 6-9 (Continued).

Initial Concentration: 372.4 μg/L
Carbon Type: F-400 (12x40) MESH
Water Matrix: Milli-Q

Elapsed Time (minutes)	Experimental Concentration (μg/L)
60.0	365.0
90.0	316.4
122.0	309.8
180.0	224.4
240.0	214.0
300.0	209.0
360.0	191.9
485.0	174.6
570.0	162.8
690.0	159.0
820.0	156.4
1275.0	160.2
1545.0	154.3
1995.0	132.2
2225.0	98.3
3140.0	85.6
4260.0	76.5
4700.0	65.0
5820.0	64.0

APPENDIX 7. MULTICOMPONENT DIFFERENTIAL COLUMN BATCH REACTOR DATA AND RESULTS

Seven components which were found in the original fresh Wausau Water were trichloroethene, tetrachloroethene, cis-1,2 dichloroethene, toluene, ethylbenzene, m-xylene, and o-xylene. A seven component equilibrium calculation using ideal adsorbed solution theory (IAST) was compared to a five component equilibrium calculation for trichloroethene, tetrachloroethene, cis-1,2 dichloroethene, toluene, ethylbenzene. Luft; 1984, developed the algorithm that was used in the IAST calculations. The initial concentrations for the m-xylene and o-xylene were 5.0 μg/L and 5.6 μg/L, respectively. At these low concentrations, the seven component and five component equilibrium concentrations were nearly identical. Therefore, a five component batch pore and surface diffusion calculation was conducted for the prediction of the multicomponent Wausau water matrix because difficulties arose when the seven component model was attempted.

Table 7-1. Batch Kinetic Data for the Multicomponent Run and (12x40) F-400 Carbon Using Fresh Wausau Water.

Carbon Type: F-400 (12X40) MESH
Water Matrix: Fresh Wausau Water
Date: 1/10/85

Elapsed Time (minutes)	Experimental Concentrations (ug/L)				
	DCE	TCE	PCE	TOL	EB
0.0	74.6	42.4	32.8	13.5	5.0
410.0	64.0	38.0	28.0	11.0	5.0
1910.0	58.0	28.0	18.0	5.0	4.0
3465.0	46.0	22.0	14.0	2.0	ND
4587.0	22.0	19.0	12.0	ND	ND
5727.0	18.0	12.0	8.0	ND	ND

ND were not detected using the Hewlett-Packard 5840A with Purge and Trap

Table 7-2 Component and System Parameters for the Multicomponent Fresh Wausau Water Run Using (12x40) F-400 Carbon

COMPONENTS:	DCE	TCE	PCE	TOL	EB
COMPONENT PARAMETERS:					
Initial Concentration; µm/L	0.7699	0.3227	0.1978	0.1465	0.0471
Freundlich Intensity Constant;(1/n)	0.5562	0.4328	0.3850	0.3282	0.2953
Freundlich Capacity Constant; K µm/g (L/µm)$^{1/n}$	46.9	192.0	435.0	475.0	714.5
Calculated Surface Diffusion Coefficient Using Equation VIII-13 10^{-10} cm^2/s	6.55	0.832	0.2315	0.1547	0.0374
Calculated Film Transfer Coefficient Using Fixed Bed Correlation; 10^{2} cm/s	1.75	1.64	1.53	1.51	1.42
Biot Number (based on pore and surface duffusion) ; (Dimensionless)	27.44	29.24	30.33	30.55	33.11
Stanton Number; (Dimensionless)	0.00315	0.00295	0.002756	0.002720	0.002558
Pore Diffusion Coefficient: 10^{6} cm^2/s	7.79	6.85	6.17	6.03	5.50
SYSTEM PARAMETERS:					
Reactor Porosity:	0.99999				
Temperature of Reactor; °C	11.0				
Superficial Velocity; cm/s	15.0				
Hydraulic Retention Time; min	15.4				
pH of Water Matrix:	6.85				
Volume of Reactor; cm^3	13150.0				
Particle Radius; cm	0.05129				
Particle Density; g/cm^3	0.8034				
Column Diameter; cm	1.1				
Wt of Carbon Used; g	0.1303				

Table 7-3. Comparison of the Multicomponent Fresh Wausau Water Data and the Predicted BPSDM Calculations.

```
                    MODEL PREDICTION vs. DATA


RESULTS FOR CIS-1,2 DICHLOROETHENE

TIME(dim)        CONC(data)      CONC(pred)      RESIDUAL

 410.000           .8579           .9738         13.51244
1910.000           .7775           .9488         22.02802
3465.000           .6166           .9338         51.44782
4587.000           .2948           .9259         ********
5727.000           .2413           .9194         ********

FMIN BASED ON    5  DATA POINTS:     FMIN = 178.94372

RESULTS FOR TRICHLOROETHENE

TIME(dim)        CONC(data)      CONC(pred)      RESIDUAL

 410.000           .8962           .9098          1.51885
1910.000           .6604           .8222         24.51027
3465.000           .5187           .7562         45.77514
4587.000           .3551           .7179         ********
5727.000           .2829           .6837         ********

FMIN BASED ON    5  DATA POINTS:     FMIN =  91.09805

RESULTS FOR TETRACHLOROETHENE

TIME(dim)        CONC(data)      CONC(pred)      RESIDUAL

 410.000           .8534           .7478         ********
1910.000           .5485           .5373         -2.05477
3465.000           .4267           .4018         -5.82380
4587.000           .3660           .3388         -7.43914
5727.000           .2437           .2903         19.12429

FMIN BASED ON    5  DATA POINTS:     FMIN =  12.37352
```

Table 7-3 (Continued). Comparison of the Multicomponent Fresh Wausau Water Data and the Predicted BPSDM Calculations.

```
RESULTS FOR TOLUENE


TIME(dim)        CONC(data)      CONC(pred)     RESIDUAL

 410.000           .8150           .6359        ********
1910.000           .3706           .3674         -.88960
3465.000           .1481           .2277        53.72225
4587.000           .0000           .1758        ********
5727.000           .0000           .1403        ********

FMIN BASED ON    5   DATA POINTS:    FMIN = *********

RESULTS FOR ETHYLBENZENE


TIME(dim)        CONC(data)      CONC(pred)     RESIDUAL

 410.000          1.0000           .6434        ********
1910.000           .8004           .0549        ********
3465.000           .0000           .0496        ********
4587.000           .0000           .0351        ********
5727.000           .0000           .0265        ********

FMIN BASED ON    5   DATA POINTS:    FMIN = *********
```

APPENDIX 8. SAMPLE INPUT AND OUTPUT FILES FOR USE WITH THE BHSDM AND THE BPSDM

The purpose of this appendix is to acquaint the potential user with the BHSDM and the BPSDM. The sample run used here is presented in figure VI-1. This appendix is broken into two parts: the BHSDM and the BPSDM sample runs. The procedure is set up in the following manner:

1. MAPPING ROUTINE
2. INPUT DATA FILE
3. PROGRAM RUNSTREAM
4. OUTPUT FILE

A. The BHSDM Sample Run

1. The computer code for the BHSDM3 (three component batch homogeneous surface diffusion model) along with code for the program GEAR were presented by Friedman (1984). The following mapping routine was used to create the absolute and relocatable elements for the BHSDM3 program.

```
@FTN,G BATCH*S.BHSDM3
@MAP,E ,BATCH*S.BHSDM3
IN BATCH*S.BHSDM3
IN BATCH*S.GEAR12
LIB MTU*FTN.
END
```

2. This was the input data for the BHSDM3 program:

```
  $DATA,
  DS = 3.1E-10,
  KF = 4.5E-3,
  CBO = 10.06,
  XK = 196.6,
  XN = .4163,
  RAD = 0.05129, RHOP = 0.8034,VOL = 4970.0, WT = 0.27587,
  EPS = 1.0E-4, DHO = 1.0E-5, NCOL = 2,
  DTO = 0.0, DSTEP =  0.5, DTOL = 8000.0,
  DOUT =  0.5, NM = 3,
  TIE=50.0,500.0,1000.0,
  TINC= 10.0,25.0,100.0,
  NDATA=34,NCOMP=1,
  &END
30.0 10.04
120.0 8.69
210.0 8.91
240.0 7.97
```

2. Input Data Continued

```
300.0 8.35
360.0 7.98
420.0 6.95
1110.0 5.33
1230.0 5.09
1350.0 4.78
1470.0 5.03
1590.0 4.35
1710.0 4.12
1950.0 3.30
2520.0 3.36
2670.0 3.50
2880.0 3.06
3150.0 2.87
3270.0 2.68
4050.0 2.68
4110.0 2.43
4230.0 2.24
4380.0 2.28
4440.0 2.18
4710.0 2.16
5490.0 2.10
5670.0 1.88
5790.0 1.72
6925.0 1.63
6045.0 1.62
6165.0 1.61
6990.0 1.67
7275.0 1.57
7665.0 1.71
```

3. The runstream was set up in the following manner:

```
@SUSPEND
@ASG,A BATCH*S.
@ASG,T 4.
@ASG,T 8.
@ASG,T 7.
@DATA,IL 4.
@ADD,PD BATCH*S.IF400/TCE
@END
@DATA,I 8.
@ADD,PD BATCH*S.10COL
@END
@XQT BATCH*S.BHSDM3
@COPY,I 7.,BATCH*S.OUT
@PRT,L BATCH*S.OUT
@RESUME,E
LOC FMIN
EXI
@ED,U BATCH*S.IF400/TCE
2
```

The collocation constants (10COL) were determined by Friedman (1984).

4. The abbreviated output file for the BHSDM3 is shown below:

```
NUMBER OF COLLOCATION POINTS, NC............ =             10
TOTAL NO. OF DIFFERENTIAL EQUATIONS, NEQ.... =             11
MASS OF ADSORBENT, WT (GRAMS)............... =     .27587+000
VOLUME OF REACTOR, VOL (CM**3).............. =     .49700+004
VOID FRACTION OF REACTOR, ECMBR (DIM.)...... =     .99993+000
RADIUS OF ADSORBENT PARTICLE, RAD (CM)...... =     .51290-001
APPARENT PARTICLE DENSITY, RHOP (GM/CM**3).. =     .80340+000
ERROR CRITERIA FOR INTEGRATION, EPS (DIM.).. =     .10000-003
INITIAL INTEGRATION STEP, DHO (MIN)......... =     .10000-004
INITIAL OUTPUT TIME, DOUT (MIN)............. =     .50000+000
TOTAL RUN TIME, DTOL (MIN).................. =     .80000+004

PARAMETERS FOR COMPONENT 1

     INITIAL BULK CONCENTRATION, CBO (MMOL/L)....... =     .10060+002
     FREUNDLICH ISO. CAP., XK (MMOL/GM)/(L/MMOL)**XN =     .19660+003
     FREUNDLICH ISOTHERM EXPONENT, XN (DIM.)........ =     .41630+000
     SOLUTE DISTRIBUTION PARAMETER, DGS (DIM.)...... =     .28359+001
     SURFACE DIFFUSION COEFFICIENT, DS (CM**2/SEC).. =     .31000-009
     FILM TRANSFER COEFFICIENT, KF (CM/SEC)......... =     .45000-002
     HOMOGENEOUS BIOT NUMBER, BIS (DIM.)............ =     .18138+002


                  MODEL PREDICTION


 ITP   TIME(min)   C(1)/CO(1)
   1       .50      .999455
   2      1.00      .998910
   3      1.50      .998365
   4      2.00      .997821
   5      2.50      .997277
   6      3.00      .996734
   7      3.50      .996191
   8      4.00      .995650
   9      4.50      .995108
   .       .           .
   .       .           .
   .       .           .
   .       .           .
 230   7400.50      .149490
 231   7500.50      .147937
 232   7600.50      .146424
 233   7700.50      .144951
 234   7800.50      .143516
 235   7900.50      .142114
 236   8000.00      .140754
```

4. Output File Continued

```
                MODEL PREDICTION vs. DATA


RESULTS FOR COMPONENT  1

TIME(dim)      CONC(data)     CONC(pred)     RESIDUAL

   30.000        .9980          .9686        -.02947
  120.000        .8638          .8893         .02949
  210.000        .8857          .8268        -.06647
  240.000        .7922          .8087         .02074
  300.000        .8300          .7755        -.06568
  360.000        .7932          .7458        -.05984
  420.000        .6909          .7188         .04052
 1110.000        .5298          .5184        -.02165
 1230.000        .5060          .4952        -.02136
 1350.000        .4751          .4739        -.00255
 1470.000        .5000          .4544        -.09114
 1590.000        .4324          .4364         .00932
 1710.000        .4095          .4199         .02517
 1950.000        .3280          .3902         .18950
 2520.000        .3340          .3337        -.00101
 2670.000        .3479          .3213        -.07636
 2880.000        .3042          .3055         .00434
 3150.000        .2853          .2872         .00684
 3270.000        .2664          .2798         .05023
 4050.000        .2664          .2393        -.10177
 4110.000        .2416          .2366        -.02033
 4230.000        .2227          .2316         .03991
 4380.000        .2266          .2255        -.00512
 4440.000        .2167          .2231         .02976
 4710.000        .2147          .2132        -.00696
 5490.000        .2087          .1892        -.09388
 5670.000        .1869          .1844        -.01323
 5790.000        .1710          .1814         .06085
 6925.000        .1620          .1575        -.02814
 6045.000        .1610          .1753         .08862
 6165.000        .1600          .1726         .07848
 6990.000        .1660          .1563        -.05836
 7275.000        .1561          .1515        -.02922
 7665.000        .1700          .1455        -.14417

FMIN BASED ON  34  DATA POINTS:   FMIN =   6.42623
```

B. The BPSDM Sample Run

1. The computer code for the BPSDM3 (three component batch pore and surface diffusion model) along with code for the program GEAR were presented by Friedman (1984). The following mapping routine was used to create the absolute and relocatable elements for the BPSDM3 program.

```
@FTN,G BATCH*PS.BPSDM3
@MAP,E ,BATCH*PS.BPSDM3
IN BATCH*PS.BPSDM3
IN BATCH*PS.GEAR40
LIB MTU*FTN.
END
```

2. This was the input data for the BPSDM3 program:

```
$DATA,
 DS = 3.1E-10,
 KF = 4.5E-3,
 CBO = 10.06,
 DP=6.43E-6,EPOR=0.641,
 XK = 196.6,
 XN = .4163,
 RAD = 0.05129, RHOP = 0.8034,VOL = 4970.0, WT = 0.27587,
 EPS = 1.0E-4, DHO = 1.0E-5, NCOL = 2,
 DTO = 0.0, DSTEP =  0.5, DTOL = 8000.0,
 DOUT =  0.5, NM = 3,
 TIE=50.0,500.0,1000.0,
 TINC= 10.0,25.0,100.0,
 NDATA=34,NCOMP=1,
 &END
30.0 10.04
...........
.Data Same.
.as BHSDM .
...........
7665.0 1.71
```

3. The runstream was set up in the following manner:

```
@SUSPEND
@ASG,A BATCH*PS.
@ASG,T 4.
@ASG,T 7.
@ASG,T 8.
@DATA,IL 4.
@ADD,PD BATCH*PS.IF400/TCE
@END
@DATA,I 8.
@ADD,PD BATCH*S.10COL
@END
@XQT BATCH*PS.BPSDM3
```

3. Runstream Continued

```
@COPY,I 7.,BATCH*PS.OUT
@PRT,L BATCH*PS.OUT
@RESUME,E
LOC FMIN
EXI
@ED,U BATCH*PS.IF400/TCE
```

4. The abbreviated output file for the BPSDM3 is shown below:

```
NUMBER OF COLLOCATION POINTS, NC............ =            10
TOTAL NO. OF DIFFERENTIAL EQUATIONS, NEQ.... =            11
MASS OF ADSORBENT, WT (GRAMS)............... =    .27587+000
VOLUME OF REACTOR, VOL (CM**3).............. =    .49700+004
VOID FRACTION OF REACTOR, ECMBR (DIM.)...... =    .99993+000
VOID FRACTION OF ADSORBENT, EPOR (DIM.)..... =    .64100+000
RADIUS OF ADSORBENT PARTICLE, RAD (CM)...... =    .51290-001
APPARENT PARTICLE DENSITY, RHOP (GM/CM**3).. =    .80340+000
ERROR CRITERIA FOR INTEGRATION, EPS (DIM.).. =    .10000-003
INITIAL INTEGRATION STEP, DHO (MIN)......... =    .10000-004
INITIAL OUTPUT TIME, DOUT (MIN)............. =    .50000+000
TOTAL RUN TIME, DTOL (MIN).................. =    .80000+004

PARAMETERS FOR COMPONENT 1

    INITIAL BULK CONCENTRATION, CBO (MMOL/L)........ =    .10060+002
    FREUNDLICH ISO. CAP., XK (MMOL/GM)/(L/MMOL)**XN. =    .19660+003
    FREUNDLICH ISOTHERM EXPONENT, XN (DIM.)......... =    .41630+000
    FILM TRANSFER COEFFICIENT, KF (CM/SEC).......... =    .45000-002
    SURFACE DIFFUSION COEFFICIENT, DS (CM**2/SEC)... =    .24500-009
    SURFACE SOLUTE DIST. PARAMETER, DGS (DIM.)...... =    .28359+001
    PORE DIFFUSION COEFFICIENT, DP (CM**2/SEC)...... =    .64300-005
    PORE SOLUTE DIST. PARAMETER, DGP (DIM.)......... =    .44284-004
    SURFACE & PORE BASED BIOT NUMBER, BIC (DIM.).... =    .16278+002

                    MODEL PREDICTION

ITP    TIME(min)    C(1)/CO(1)
  1        .50       .999455
  2       1.00       .998910
  3       1.50       .998365
  4       2.00       .997821
  5       2.50       .997277
  6       3.00       .996734
  7       3.50       .996192
  8       4.00       .995650
  9       4.50       .995109
  .         .           .
  .         .           .
  .         .           .
230    7400.50       .152406
231    7500.50       .150882
232    7600.50       .149398
233    7700.50       .147950
```

4. Output File Continued.

```
                 MODEL PREDICTION vs. DATA

        RESULTS FOR COMPONENT  1

        TIME(dim)      CONC(data)     CONC(pred)     RESIDUAL

           30.000         .9980          .9688        -.02931
          120.000         .8638          .8903         .03063
          210.000         .8857          .8281        -.06501
          240.000         .7922          .8100         .02240
          300.000         .8300          .7768        -.06417
          360.000         .7932          .7468        -.05849
          420.000         .6909          .7197         .04170
         1110.000         .5298          .5167        -.02474
         1230.000         .5060          .4934        -.02493
         1350.000         .4751          .4720        -.00658
         1470.000         .5000          .4525        -.09509
         1590.000         .4324          .4344         .00471
         1710.000         .4095          .4179         .02034
         1950.000         .3280          .3883         .18387
         2520.000         .3340          .3324        -.00478
         2670.000         .3479          .3203        -.07945
         2880.000         .3042          .3047         .00170
         3150.000         .2853          .2868         .00527
         3270.000         .2664          .2795         .04913
         4050.000         .2664          .2400        -.09927
         4110.000         .2416          .2374        -.01729
         4230.000         .2227          .2324         .04381
         4380.000         .2266          .2265        -.00059
         4440.000         .2167          .2242         .03478
         4710.000         .2147          .2146        -.00066
         5490.000         .2087          .1911        -.08434
         5670.000         .1869          .1865        -.00192
         5790.000         .1710          .1836         .07366
         6925.000         .1620          .1602        -.01112
         6045.000         .1610          .1776         .10317
         6165.000         .1600          .1750         .09354
         6990.000         .1660          .1591        -.04160
         7275.000         .1561          .1544        -.01079
         7665.000         .1700          .1485        -.12658

        FMIN BASED ON  34  DATA POINTS:    FMIN =    6.33310
```